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BATTELLE'S

FINAL REPORT

On

R&D STATUS OF

CARBON DIOXIDE

SEPARATION,

DISPOSAL, AND

UTILIZATION

TECHNOLOGIES

April 25, 1991



Battelle

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DISPOSAL, AND UTILIZATION TECHNOLOGIES

to

TRANSALTA UTILITIES CORPORATION

April 25, 1991

by

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EXECUTIVE SUMMARY

Background, Objectives, and Approach

Carbon dioxide is a greenhouse gas that contributes to global warming. There is increasing interest in technologies to capture carbon dioxide economically and either use it effectively or dispose of it on a cost/effective basis.

A consortium of Canadian organizations recognized that the first step in being prepared to control carbon dioxide is a preliminary delineation of the state of the art. The key questions are:

- What has really been accomplished in technologies that relate to the capture, disposal, and use of carbon dioxide?
- How strong are the current efforts by others to solve the technological problems?
- Which areas should be the subject of active research and development by Western Canada, given its geographical location and natural resources?

This report is the outcome of an initial investigation by Battelle. The approach included literature research and interviews, but no technical research.

Highlights of the Study

- (1) Capture of carbon dioxide from power plants and industrial boilers with the conventional MEA flue gas scrubbing technology is currently technically feasible, but inordinately expensive for coal-fired plants. High quality natural gas has better prospects.
- (2) For new large power plants, the integrated gasification combined cycle (IGCC) designs do provide the opportunity to capture carbon dioxide economically and in a form that is ready for transportation to utilization/disposal sites. The costs are higher than for facilities without CO₂ emission controls but they do not appear to be prohibitive.
- (3) Most of the power plants and large industrial boilers that will be in service in 2005 are in place now. Thus, IGCC technology is not a solution for 70 percent of the expected capacity.
- (4) The best retrofit technology that we have found is the flue gas recycle combustion technology. The combustion of fuel in a mixture of oxygen and carbon dioxide yields a flue gas that is about 95 percent carbon

dioxide and which needs little cleanup prior to transportation for enhanced oil recovery or other high volume uses that can accept moderate purity.

- (5) The cost of steam and power from the flue gas recycle process is highly dependent on the cost of oxygen. Technological improvements in oxygen manufacture merit high priority. Also, optimization of the oxygen percentage in the combustion air without undue compromise in combustion performance and in the transportation and end use stages is a high priority item.
- (6) The idiosyncracies of individual boilers could confound the evaluation and commercialization of the flue gas recycle combustion technology. Therefore, new facilities, rather than retrofits, are needed to demonstrate this technology.
- (7) The enhanced oil recovery (EOR) end use appears to be the best means of utilization/disposal for western Canada.
- (8) Use of Elk Point Basin brines for disposal of carbon dioxide is an attractive research area. There are many technical problems, but the rewards of having a resource that could absorb carbon dioxide as magnesium and/or calcium carbonates for geological time periods makes it worthwhile to devote attention to this area.
- (9) The cold climate of specific sites in this region of Canada may be a major advantage in addressing the carbon dioxide problem. A thermal swing absorption process for oxygen production that requires a temperature of 40 F may be highly economical in Canada and not feasible in warmer climates. It may even be possible to store carbon dioxide as the hydrate, using snow and moderate pressure to make "carb-ice".
- (10) Accountability for annual performance in carbon dioxide capture is needed for success of concepts that are based on cold climate technology. The Consortium should resist regulations that require compliance with short term emission standards.
- (11) There are interesting utilization routes that involve using CO₂ to produce polymers and construction materials. They are of interest to companies that can take advantage of the forthcoming low-cost, high-volume supply of carbon dioxide. Their priority is not as high as the items described above for contributing to reduction in carbon dioxide emissions.
- (12) The attempt to capture and transport carbon dioxide leads to ultimate production of more carbon dioxide than would be made otherwise. Therefore, effective disposal and/or utilization is essential.

FINAL REPORT
on
**R&D STATUS OF CARBON DIOXIDE SEPARATION,
DISPOSAL, AND UTILIZATION TECHNOLOGIES**

INTRODUCTION

Global warming has become a critical international issue. Suggestions of "carbon taxes" and subsidies for energy options that promise to reduce the generation of greenhouse gases are occurring before the technological options have been explored adequately. The system dynamics by which carbon dioxide is emitted into the atmosphere, captured in oceans and on land, stored, and re-emitted are so poorly understood that simple materials balances do not close for the major models used in forecasting global warming. Billions of tons of carbon dioxide "vanish" each year. A global warming problem may exist, but its magnitude and timing are problems that may take years to solve.

The carbon dioxide problem is so difficult in part because carbon dioxide is present in air at low concentration (0.03 percent) and conventional facilities make flue gases that contain only 8 percent to 20 percent carbon dioxide. Low concentration is only part of the problem. The physical properties of carbon dioxide are not conducive to easy storage and its reactivity is limited so that huge end uses are not apparent, even if the price of carbon dioxide were reduced to zero.

In the meantime, there is a very real issue of development of technologies to capture carbon dioxide, use it, and/or dispose of it. Processes for capture, use, and disposal require substantial lead times for development, demonstration, cost reduction, and market penetration. Those responsible for using technology to ameliorate the carbon dioxide greenhouse gas problem cannot wait for a crisis to begin to solve this problem. The scientific and technological problems require a systematic approach, and more than one solution will be needed to accommodate the variety of circumstances in which carbon dioxide is generated and environments in which it can be stored or used.

A consortium of Canadian organizations decided to have a study made of the state of the art for controlling CO₂ emissions and to identify the opportunities to make progress in the development of technologies to capture carbon dioxide, use this compound where feasible, and dispose of it in ways that do not increase global warming.

Battelle was selected to conduct a brief project to attain the above objectives. The workplan for the study (Figure 1) reflects the use of literature research and interviews with knowledgeable respondents. A database was prepared as part of the project. It is listed in alphabetical order by first author in Appendix A of this report. Thus, it serves as a List of References. Each client is also receiving a computer disk with an Excel® database on it.

CONCLUSIONS

This section of the report summarizes the salient points of the investigation. The reader is referred to the Discussion Section and Appendices for details.

State of the Art

The systems that will be successful generally include capture and disposal. Utilization is reviewed separately in this study; even though it is a special case of disposal.

Carbon Dioxide Capture

For new facilities, the Integrated Gasification Combined Cycle (IGCC) power plant provides a relatively concentrated carbon dioxide stream. This stream is suitable for capture by physical solvent scrubbing systems, such as the Selexol process. It appears that the cost of electricity is increased less than 15 percent by this system, whereas conventional pulverized coal (PC) plants with amine scrubbers are much more expensive.

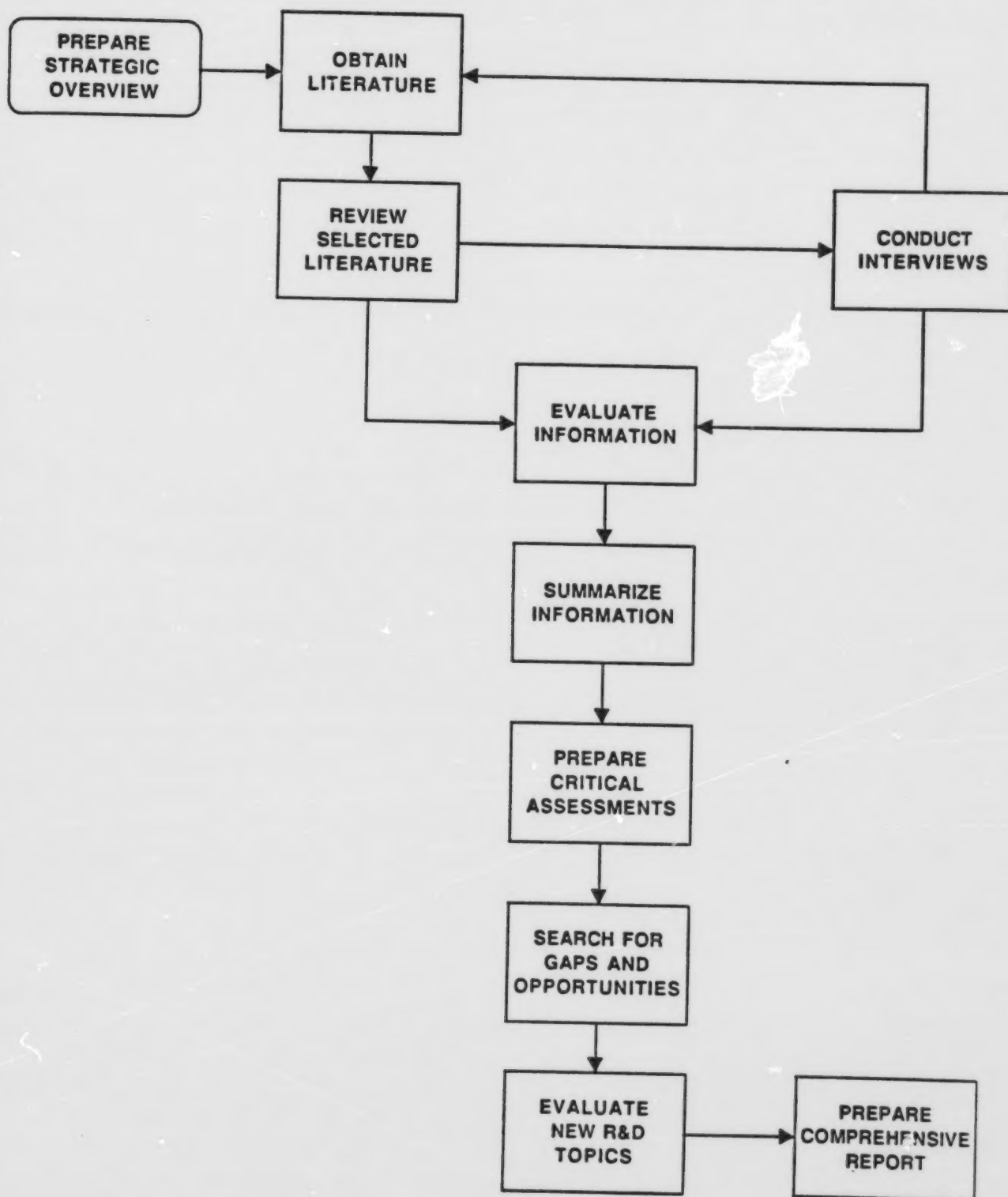


FIGURE 1. WORKPLAN FLOWCHART

The flue gas recycle combustion system sidesteps the scrubbing step by generating an effluent gas that is about 95 percent carbon dioxide. This approach is a front runner for retrofit of pulverized coal facilities and may be second to the IGCC approach for new plants. Oxygen costs are a major factor impeding commercialization. A major cost factor for this option is that existing power plants have to be extensively refitted to correct gas leaks.

The HYDROCARB system obtains the hydrogen that is in the fossil fuel and conserves the carbon that is left over. The amount of fuel credit per ton of coal is less than obtained in the primary combustion of coal, but carbon dioxide emissions are greatly reduced. The concept is soon to be tested at the pilot plant scale.

Disposal

The line between disposal and utilization is a fine one. We consider that a process that immobilizes carbon dioxide such that it does not re-enter the atmosphere within a short time span is a disposal option. The disposal activity includes the operations that are required to transport the carbon dioxide to the immobilization site and the cost for transporting the immobilized CO₂ to a disposal site. Disposal incurs costs whereas utilization brings forth revenues. However, many utilization paths lead promptly back to the atmosphere.

The major alternative disposal schemes are:

- (1) Deep ocean
- (2) Injection into geological formations, especially abandoned gas or oil wells
- (3) Conversion of brines to insoluble carbonates
- (4) Immobilization in glassy matrices, especially gas hydrates.

Oceans appear to have a great capacity for storing carbon dioxide in the depths. The surface layers are saturated with carbon dioxide, so it does appear that the depths are needed for storage. At great depths, carbon dioxide would probably exist as insoluble solid inclusion compounds (CO₂ hydrates). The fate and effects of storage of

carbon dioxide at great depths are just now beginning to be investigated in the United States and in Japan.

Battelle cannot endorse deep ocean disposal of carbon dioxide because the fate and effects of this strategy are open to serious question. Both FPRI and DOE are approaching this solution to the disposal with considerable reservations and caution.

Because carbon dioxide does form an inclusion compound with water when pressure is applied, there are opportunities to store carbonated ice in the colder regions of Canada. Enhancement of the stability of this inclusion compound is a stimulating challenge, especially since its decomposition appears to be controllable by macro-fabrication techniques.

Abandoned gas or oil wells have many good features in that the ones selected for disposal of carbon dioxide can withstand considerable pressure and already have holes drilled and other infrastructure. The Client Consortium is already aware of this disposal method and its pros and cons. There are questions regarding the possibility of leakage of gas but this does not appear significant, when the local geology homework has been done properly.

The Elk Point Basin of Western Canada has brines that are rich in magnesium and/or calcium. These alkaline earth compounds could be converted to carbonates that could be stored for geological time periods. Some fraction of these carbonates could be made for conversion to useful chemicals and materials. This aspect is covered in the Utilization section of this report.

This Brines Process appears to be quite attractive in storing the carbon dioxide for periods of time that are measured in millennia, not minutes or months. However, the balanced equations indicate that there is likely to be large amounts of hydrochloric acid made as the carbonates are made. We believe that the technical difficulties can be overcome if considerable costs can be incurred; however, we are not sure whether the improvements will be viable on the disposal scale with its need to be of minimal cost.

Disposal technologies frequently require that the carbon dioxide or immobilized CO_2 be transported considerable distances. There is experience with pipelines that

use supercritical carbon dioxide (Farris, 1983). Although the problems appear to be solvable, the costs can be enormous, as indicated in a recent EPRI study that was conducted by Fluor Daniel (Smelser and Booras, 1990).

Utilization

The generation of carbon dioxide from fossil fuels is roughly 1000 times the consumption in current applications. In our opinion, the utilization of carbon dioxide will grow dramatically over the next decade but without significant breakthroughs in economic utilization routes, capture and disposal of carbon dioxide will have negligible impact on the global warming issue. However, the availability of carbon dioxide in large quantities and at low prices can provide profitable and environmentally desirable business opportunities. Typically, we would expect that utilities could sell or give their effluents to customers who may use some and dispose of the rest.

Enhanced oil recovery provides a market for carbon dioxide while the greenhouse gas is being buried. The specifications for gases to be used in EOR may necessitate the cleanup of some captured carbon dioxide. This end use also can tolerate some amount of impurities. EOR is one of the most desirable large scale carbon dioxide uses for Western Canada as the oil fields are located near the power plants. Applications in tar sands and gas production may also be developed. The amount of carbon dioxide that is needed diminishes as the petroleum flow from carbon dioxide flooding proceeds because the gas can be recovered and reinjected at the well head.

Natural gas storage wells need "cushion gas" that is usually just part of the gas that is stored. There is an opportunity to use carbon dioxide as a cushion gas. GRI has technology to separate CO₂ from the natural gas stream just before pipelining. This approach conserves natural gas at the same time that it disposes of carbon dioxide.

Use of Western Canadian brines for production of magnesium carbonate or bicarbonate opens the way to several chemical and materials business opportunities. Differences between this utilization opportunity and disposal opportunities is one of scale and close control of the properties and quality of the carbonate products.

Conventional refrigeration markets for dry ice are already saturated. There is a move to replace CFC-based refrigerator systems with liquid ammonia. Good reasons to use carbon dioxide instead of ammonia are not apparent. There may be additional refrigeration markets developed but they are not likely to be attractive in terms of the quantities that are generated by power plants.

Biomass can soak up great quantities of carbon dioxide and hold it for various time periods. Wood in trees can hold carbon dioxide for decades or centuries. The trees can be converted into lumber, fiberboard products or other materials with long lifespans. However, it is difficult to force-feed forests from a power plant.

Algae can use waste heat, carbon dioxide, and brackish water to produce biomass that can store carbon dioxide or be converted to other products. The waste heat from steam plants can also be combined with fresh water and carbon dioxide to generate high value biomass in greenhouses.

There are interesting utilization routes that involve using CO₂ to produce polymers and construction materials. They are of interest to companies that can take advantage of the forthcoming low-cost, high-volume supply of carbon dioxide.

Major Non-Canadian Players in CO₂ Development

The activities of the major players in the international debate and development on global warming are still focused primarily on assessment of the problem rather than development of hard technology. In this section of the report, some of the development activities are discussed.

United States

The United States government has taken the position that reduction in emissions of carbon dioxide through use of more efficient combustors and energy conservation is the preferred route to reduction of carbon dioxide emissions. There are a

few major developers of carbon dioxide emission control technology in the United States and some signs that the U.S. government is shifting its position.

The Gas Research Institute (GRI) in Chicago has the most highly organized program in this general area. They prepare and publish Five Year Plans that are updated annually. As shown in Table 1, they are spending about \$21 million on topics that are at least somewhat related to the ones under consideration in this study. This is about 10 percent of their total budget.

GRI is developing new methods to contact gases with capturing agents in which centrifugal force is used. They are developing hybrid capture processes in which amines and membranes cooperate. They also have considerable work in underground storage. GRI is a major source of funding for basic research that concerns transport phenomena and non-ideal gas properties.

EPRI's research and development was focused on the Cool Water IGCC in the past. Fluor Daniel is still investigating the costs and engineering involved in carbon dioxide capture and disposal. Biomass is another area of interest to EPRI for carbon dioxide disposal. They are concerned about the ecological consequences of deep ocean dumping and have projects to investigate the phenomena involved.

Up to now, there has been little U.S. Department of Energy action on topics other than simulations and data gathering for simulations of global warming futures. Considerable funds are expended on these topics that involve heavy use of weather satellites and supercomputers--about \$1,000 million per year.

The Pittsburgh Energy Technology Center (PETC) has developed a draft strategy for technological research and development. The plan will be subject to various political constraints, but is likely to represent a substantial investment within the ongoing program entitled "Flue Gas Cleanup". The strategy will be announced formally at the Air and Waste Management Association Conference this spring. It includes systems studies, long term studies, and mid range programs. Solid targets are not delineated yet. EPA is planning to fund construction of a pilot plant for the HYDROCARB process.

TABLE 1. RELEVANT GAS PROCESSING R&D BY GRI AND OTHERS

AREA	\$1000 per Year						
	1989	1990	1991	1992	1993	1994	1995
TOTAL RELEVANT R&D	12,898	13,140	20,707	21,257	21,342	21,007	20,975
Advanced Gas Processing, total	1,213	3,265	8,040	8,890	8,960	8,730	8,580
GRI	750	2,700	4,550	4,650	4,700	4,700	4,700
Government	0		200	600	600	250	0
Industry	463	565	3,290	3,640	3,660	3,780	3,880
Relevant 1991 projects, total	0	0	6,360	0	0	0	0
Contacting/Separation Devices			410				
Separation of Nitrogen Gas			2,000				
Acid Gas Removal			3,950				
Gas Storage Technology, total	1,550	1,000	1,000	1,100	1,100	1,100	1,100
GRI	1,100	900	900	900	900	900	900
Government	0	0	0	0	0	0	0
Industry	450	100	100	200	200	200	200
Relevant 1991 projects, total	0	0	1,000	0	0	0	0
Improve Cushion Gas and Foaming			1,000				
Advanced Gas Separation, total	1,040	1,177	4,107	3,867	3,877	3,977	4,095
GRI	970	970	3,150	2,850	2,850	2,950	3,050
Government	0	50	370	380	390	390	390
Industry	70	157	587	637	637	637	655
Relevant 1991 projects	0	0	3,917	0	0	0	0
Gas Separation Technology			600				
Gas Separation Science			607				
Fluid Properties			2,150				
End-Use Processes and Equipment			560				
Heat and Mass Transport, total	1,300	1,450	1,800	1,850	1,850	1,750	1,900
GRI	1,000	1,000	1,300	1,350	1,400	1,400	1,400
Government	300	450	500	500	450	350	500
Industry	0	0	0	0	0	0	0
Relevant 1991 projects, total	0	0	600	0	0	0	0
Sorption Materials and Processes			600				
Methane Reaction Science, total	3,425	3,668	4,460	4,250	4,255	4,150	4,150
GRI	2,305	2,485	2,585	2,500	2,655	2,600	2,600
Government	220	625	850	850	450	450	450
Industry	900	558	1,025	900	1,150	1,100	1,100
Relevant 1991 projects, total	0	0	1,150	0	0	0	0
Chemical Reactions			950				
Metal Oxide Reduction Chemistry			200				
Properties Research, total	4,370	2,580	1,300	1,300	1,300	1,300	1,150
GRI	1,300	1,150	700	700	700	700	700
Government	2,770	1,080	300	300	300	300	200
Industry	300	350	300	300	300	300	250
Relevant 1991 projects, total	0	0	1,300	0	0	0	0
Thermophysical Properties of Gases			650				
Fluids in Micropores			650				

Japan

The goal of the Japanese government is to keep carbon dioxide emissions in the year 2000 at the same level as occurred in 1990, despite population growth of 10 million people. Current carbon dioxide emissions per capita are 2.5 tons per year. MITI has a strong research, development, and engineering campaign underway. Major electric companies (e.g., Tokyo Electric) and engineering companies (e.g., Mitsubishi Heavy Industries) are believed to be involved. Publications and discussions indicate that deep ocean disposal is high on the list of approaches to disposal in the MITI program.

Japan is leading the world in development of carbon dioxide capture, disposal, and utilization at the present time. CRIEPI, Mitsubishi, and others in Japan are believed to be undertaking major R&D and demonstration projects. In addition, their basic research is strong. As examples, a researcher has found a copper complex that can remove carbon dioxide from ambient air that contains only 0.03 percent carbon dioxide (New Scientist, 1990). Another Japanese researcher has found a way to react carbon dioxide with an iron oxide to obtain carbon and an oxygen-enriched iron oxide (Tamura and Tabata, 1990). Many new systems for capturing carbon dioxide will only succeed in the market place if the cost of oxygen is reduced. The Japanese research establishment is also strong in cost reduction for oxygen.

Combustion technology is a key to control of carbon dioxide emissions. One approach is the production of oxygen by more efficient or effective means. The thermal swing method (page 75) is an example of this approach by a Japanese company. Major Japanese companies have been following closely the flue gas recycle combustion technology. At least one is believed to be making improvements on this approach.

The emphasis is on rendering the costs of capture and disposal as low as possible. The economical utilization of large quantities of carbon dioxide still has not been achieved in Japan. As the inventors and developers of polycarbonates that are made directly from gaseous carbon dioxide, there are substantial efforts in this area. Mitsui is introducing one of these polycarbonates for use as a biodegradable plastic, a use that would return its carbon dioxide to the atmosphere rapidly.

Europe

European research has been discussed in some detail at the OECD/IEA Experts' Seminar in Paris in 1989. The University of Utrecht is an outstanding research and development center so far as the IGCC approach to reducing carbon dioxide emissions and easing the capture of this effluent. They are also studying the disposal methods, especially the use of abandoned wells. Shell International is also very active in evaluation of IGCC and abandoned wells in the Netherlands (Wolters, 1990).

In Italy, the emphasis is on chemical production from carbon dioxide (Aresta, 1989). C_1 chemicals are the principal objectives, although many fine chemicals are also under consideration. Thus, methanol and its transformation products are to be made from carbon dioxide and hydrogen. The problem of how to manufacture the cheap hydrogen remains unanswered in Europe, as in Japan and North America.

The European activities include the biomass work at University College, London. One can expect the major European and Scandinavian engineering companies to be in the forefront of sale of scrubbing and other carbon dioxide abatement systems.

Promising Targets

The interests of the Client Consortium are quite varied; therefore, the targets that would be considered promising depend on the orientation of the specific organization. The following list has something for everyone.

- (1) Construction of an IGCC power plant can reduce carbon dioxide emissions by the higher efficiency of the facility and by capture of carbon dioxide made by the shift reaction. It is a safe investment in responsible control of carbon dioxide emissions, but it is costly compared with other power plants that ignore environmental considerations. Because the acid gases are separated with sulfur recovery, the quality of the carbon dioxide can be quite high. Capture of carbon dioxide with a Selexol Process probably will not be costly.

- (2) Because more than 70 percent of Western Canada's power plants of the year 2005 are already in place (Alberta Energy, 1990), it follows that retrofits will be the major opportunity to reduce carbon dioxide emissions. The flue gas recycle combustion capture process can be used to retrofit existing power plant or industrial boiler systems. No sulfur removal step or acid gas cleanup is required, providing that disposal in abandoned wells is contemplated. Cleanup may be needed for other uses, depending on the composition of the combustion products.
- (3) The Client Consortium and others are already considering EOR as the principal utilization scheme and should proceed with this activity.
- (4) The magnesium/calcium brines provide Western Canada with the opportunity to manufacture an array of inorganic chemicals and materials while disposing of carbon dioxide. This is a major area in which to innovate, however, conventional approaches probably will not work.
- (5) Improvements in the production of oxygen are quite relevant to low cost carbon dioxide capture because both the IGCC and the flue gas recycle combustion processes have oxygen as an important cost element. A temperature swing process for oxygen separation from air may be attractive in the colder regions of Canada because the need for a chiller and the electricity to operate the chiller would be greatly reduced in Western Canada. Improvement of this process is a promising target for colder regions of Canada and countries having similar climates.
- (6) Polymers that are derived ultimately from carbon dioxide are under investigation by Battelle as storage vehicles for carbon dioxide. The polymers have potential industrial use and also have a long storage life.

A Cautionary Note

Consider two energy-producing technologies, one of which allows carbon dioxide to escape to the atmosphere and the other endeavors to capture the carbon dioxide, transport it, and store or utilize it. For all technologies that we have found to date, the attempt to tame carbon dioxide results in a greater production of this substance than occurs otherwise. Therefore, disposal and/or utilization had better be good or we are worse off than if we ignored the problem.

CRITICAL ASSESSMENTS

The following opportunities have been chosen for critical assessment, based on their potential to contribute to reduction of carbon dioxide emissions in a cost-effective manner:

Avoidance Methods

- HYDROCARB
- Flue Gas Recycle Combustion

Capture Methods

- Amine Scrubbing
- Refrigeration
- Membrane Permeation
- Biomass Growth
- Temperature Swing Absorption of Carbon Dioxide

Disposal of Captured Carbon Dioxide

- Abandoned Wells
- Reaction with Brines
- Deep Ocean
- Reservoirs with Brackish Water

Utilization Opportunities

- EOR
- Brine Chemicals
- Polymers
- Construction Materials
- Biomass Products.

Avoidance Methods

Emission of carbon dioxide can be avoided by not using carbonaceous fuels, by reducing the amount of fuel that is needed to meet the demand for energy, reducing the demand for energy by changing our society, by using a carbonaceous fuel that is combusted to some product other than carbon dioxide, or by altering the combustion process so that carbon dioxide is a major constituent of the flue gases. The scope of this investigation includes only the last two of the possibilities.

Fuel cells, coal-fired MHD, and photovoltaics are typical technologies that deserve separate studies similar to this one. They improve the global warming situation by using more efficient, non-carbon dioxide-generating methods. Discussion of these technologies is beyond the scope of this study.

Combustion of fossil fuels without consuming carbon has been studied by Steinberg and his associates for several years (Steinberg and Grohse, 1988, 1989, 1990). The origin of a flue gas recycle combustion process that yields a flue gas that is about 95 percent carbon dioxide is shrouded in mystery. However, it is clear that Argonne National Laboratory is the primary advocate and source of information on this approach (especially Wolsky, et al., 1990).

HYDROCARB Process

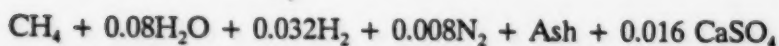
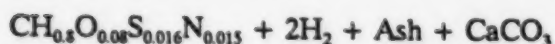
The basic concept of this process is presented on Table 2 (Steinberg, 1989). We developed a simple schematic of the steps in the process (Figure 2); the original literature has detailed conceptual flow sheets. An example is provided in Figure 3.

TABLE 2. HYDROCARB (CARBEX) PROCESS FOR PRODUCTION OF ASH-FREE AND SULFUR-FREE CLEAN CARBON FUEL (CARBOLINE) AND FUEL GAS FROM COAL

Two Basic Steps:

I. Hydrogasification of Coal with Hydrogen to Methane

Bituminous Coal + Hydrogen → Methane + Water + Hydrogen + Ash



Reaction is -18 Kcal/mol Exothermic

II. Thermal Decomposition of Methane

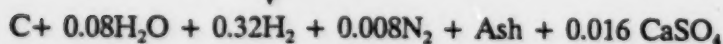
Methane → Carbon Black + Hydrogen



Reaction is +18 Kcal/mol Endothermic

Hydrogen is recycled. Excess hydrogen is a by-product and is used as fuel, and carbon black is used neat slurried with water, methanol, or oil to produce CARBOLINE CWM fuel product.

OVERALL COAL CRACKING REACTION



Source: Meyer Steinberg, "An Option for the Coal Industry in Utilizing Fossil Fuel Resources with Reduced CO₂ Emissions", Report No. BNL-42228-Rev., DE89 015021, May 1989, under Contract No. DE-ACO2-76CH00016.

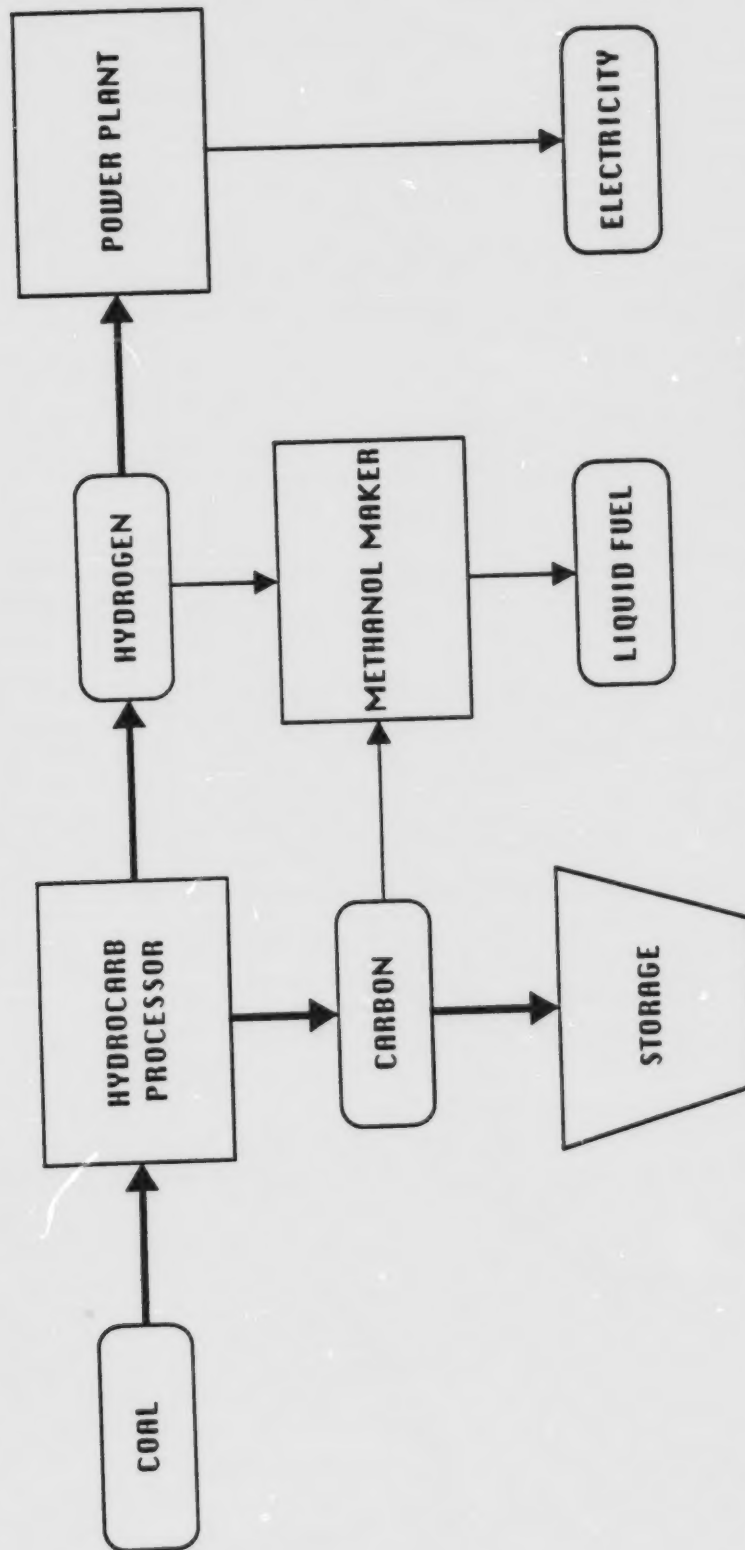


FIGURE 2. HIGHLY SCHEMATIC HYDROCARB® PROCESS FLOWSHEET

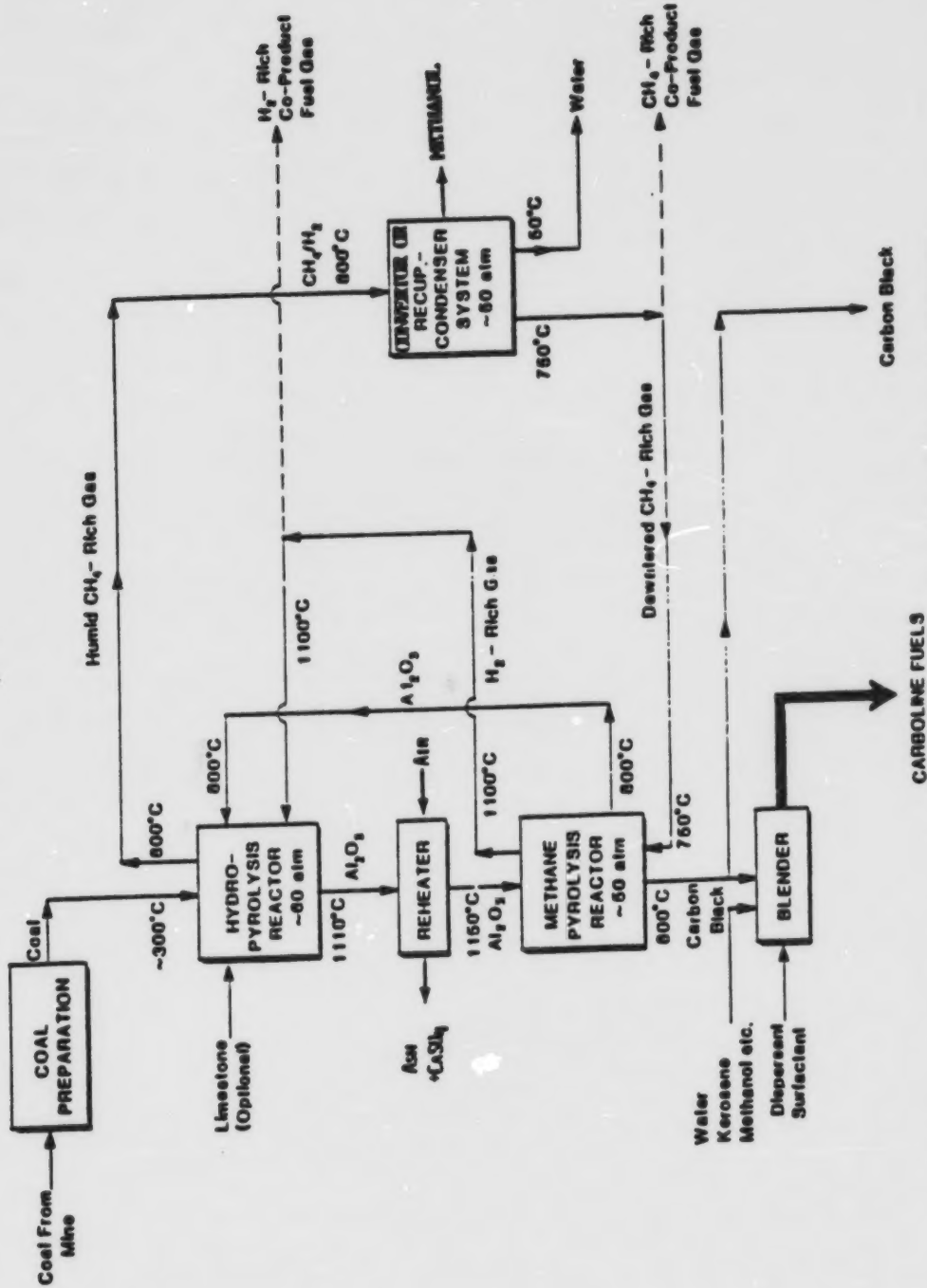


FIGURE 3. MORE DETAILED HYDROCARB® PROCESS FLOWSHEET

Source: Steinberg, M. and Grohse, E.W., November 1990.

This process is designed to make use of the energy neutrality of the combination of the two reactions. That is, the first step is exothermic and second step is endothermic to about the same extent.

The process has been evaluated by Brookhaven on the rack scale by operating the two major steps independently. A rack scale facility is one that is bigger than bench but not too large to fit into a laboratory. Typical coals have been hydrogenated in an entrained tubular reactor with commercial hydrogen. Separately, commercial methane has been pyrolyzed to yield hydrogen and carbon. The U.S. EPA is planning to fund a pilot plant to bring the two steps together. We estimate that the pilot plant program will be a multimillion-dollar effort.

As is necessary before pilot plant data are available, the Brookhaven group have made estimates and extrapolations to obtain preliminary estimates of the cost of the fuels made by this process. They have provided some detailed process flowsheets to Battelle and also have developed process equipment lists and capital cost estimates from those lists.

Many different feedstocks have been subjected to this economic analysis that uses both utility financing and industrial financing. An example flowsheet for the process is shown in Table 3. The calculated costs of methanol prepared using this process are so attractive that there is either a breakthrough or a problem with the assumptions/calculations.

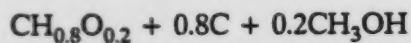
Unfortunately, a detailed, integrated mass and energy balance has not been published for the HYDROCARB process. The reason that we are concerned is that most carbonaceous feedstocks do not have enough hydrogen both to generate the methane for use in hydropyrolysis and to make significant amounts of the energy-rich end products (hydrogen and carbon black).

Brookhaven may be willing to supply the Client Consortium with the details that are needed to become enthusiastic about the process. In any event, the EPA pilot plant studies should lead to an ultimate resolution of this problem.

When operated in a true avoidance mode in which only the hydrogen is used and the carbon black is stored in the ground, coal or lignite provide only 11 percent to 40

TABLE 3. ESTIMATE OF HYDROCARB CARBON FUEL PLANT WITH METHANOL AS CO-PRODUCT

PLANT: Montana Lignite - 45% C - 25,000 T/D



PRODUCTION = 90% Efficient - 90% Plant Factor - \$0.8 Billion

$$\text{Carbon} = 0.8 \times 0.45 \times 0.90 \times 25,000 = 8,100 \text{ T/D}$$

$$\text{Methanol} = 0.2 \times 0.45 \times 0.90 \times 25,000 \times \frac{32}{12} = 54,400 \text{ T/D}$$

$$\text{BBl/Day} = \frac{5,400}{0.138} = 39,000 \text{ BBl/Day}$$

PRODUCTION COST

	<u>\$/Day</u>
Lignite + 25,000 x \$10/T	= \$250,000
O&M	= 110,000
F.C. = $0.219 \times \frac{0.8 \times 10^9}{328.5}$	= <u>533,000</u>
Total	\$893,000
Credit for Carbon Fuel $\frac{\$2.50}{\text{MMBTU}} \times 28.2 \text{ MMBTU} \times 8100/\text{T}$	= <u>571,000</u>
Net Daily Cost	\$322,000
Methanol Selling Price = $\frac{322,000}{39,200} = \$8.20/\text{Bbl}$	= <u>\$0.20/gal</u>
If Carbon Credit at \$3.00/MMBTU Methanol S.P.	= <u>\$0.13/gal</u>

Source: M. Steinberg, E.W. Grohse, "Production of Clean Carbon Fuel and Co-Product Gaseous or Liquid Fuel from Coal: The Hydrocarb Process", Brookhaven National Laboratory.

percent of the energy that could be sent to customers, compared with 100 percent for conventional combustion (Table 4).

In addition to possible use of HYDROCARB to make methanol, Brookhaven has also been evaluating the carbon black from this process for slurry fuel applications with some interesting results.

The HYDROCARB process could make its initial debut by manufacturing hydrogen, carbon black, slurry fuels and other products from a locally attractive combination of natural gas and coal feedstocks. Pyrolysis of the natural gas provides plenty of hydrogen for hydrogasification and contributes some of the carbon product.

Flue Gas Recycle Combustion. Avoidance approaches to solving the carbon dioxide problem can include technologies that avoid the need to capture and concentrate the carbon dioxide stream, as well as those that avoid the initial production of the carbon dioxide. The term "as well as" is not quite accurate because this type of avoidance still requires that successful uses and/or disposal technologies become available!

Since 1982, Argonne National Laboratory has been developing a process to recover carbon dioxide from the flue gas that results from burning coal in a mixture of oxygen and recycled flue gas. This process raises the CO_2 level with flue gas to 90+ percent, making CO_2 recovery attractive. Figure 4 is a simple schematic of this process. More detail and some early energy balance calculations by Steinberg are shown in Figure 5.

This development has been supported by a series of studies that have been conducted by Argonne itself, Battelle, Environmental and Energy Research, and others. The investigations have included small-scale combustion research, scale-up to a 50 MW plant, and several computer simulation studies that made use of the data provided by the experimentalists. The modeling studies provided projected data regarding gas phase fluid dynamics, convective and radiative heat transfer, and other aspects of the combustion process. Plant efficiencies that rival or even surpass conventional combustors appear possible, when the carbon dioxide/oxygen ratio and the combustion conditions are optimized.

TABLE 4. REDUCING CO₂ EMISSIONS FOR MITIGATING THE CO₂ GREENHOUSE EFFECT
THERMOCHEMISTRY OF FOSSIL FUEL CRACKING BY HYDROCARB SYSTEM

Fuel Type	Derived Fuel	Combustion Emission		
		Emitted C/H as CO/H ₂ /H ₂ O	Lb CO ₂ MMBTU	Energy Available, %
Coal CH _{0.4} O _{0.08}	1.00 C + 0.32 H ₂ + 0.08 H ₂ O	0.00	0	19
	0.96 C + 0.40 H ₂ + 0.04 CO ₂	0.05	40	24
	0.84 C + 0.16 CH ₄ + 0.08 H ₂ O	0.25	120	29
	0.76 C + 0.20 CH ₄ + 0.04 CO ₂	0.30	140	37
	0.92 C + 0.08 CH ₃ OH + 0.24 H ₂	0.01	60	27
Lignite CH _{0.4} O _{0.02}	CO ₂ + 0.4 H ₂ O	1.25	210	100
	1.00 C + 0.18 H ₂ + 0.22 H ₂ O	0.00	0	11
	0.89 C + 0.40 H ₂ + 0.11 CO ₂	0.14	100	24
	0.91 C + 0.09 CH ₄ + 0.21 H ₂ O	0.25	120	17
	0.69 C + 0.20 CH ₄ + 0.11 CO ₂	0.39	180	38
Combustion	0.78 C + 0.22 CH ₃ OH	0.25	130	35
	CO ₂ + 0.4 H ₂ O	1.25	220	100

Source: M. Steinberg and E.W. Grohse, "Production of Clean Carbon Fuel and Co-Product Gaseous or Liquid Fuel from Coal: The Hydrocarb Process", Brookhaven National Laboratory.

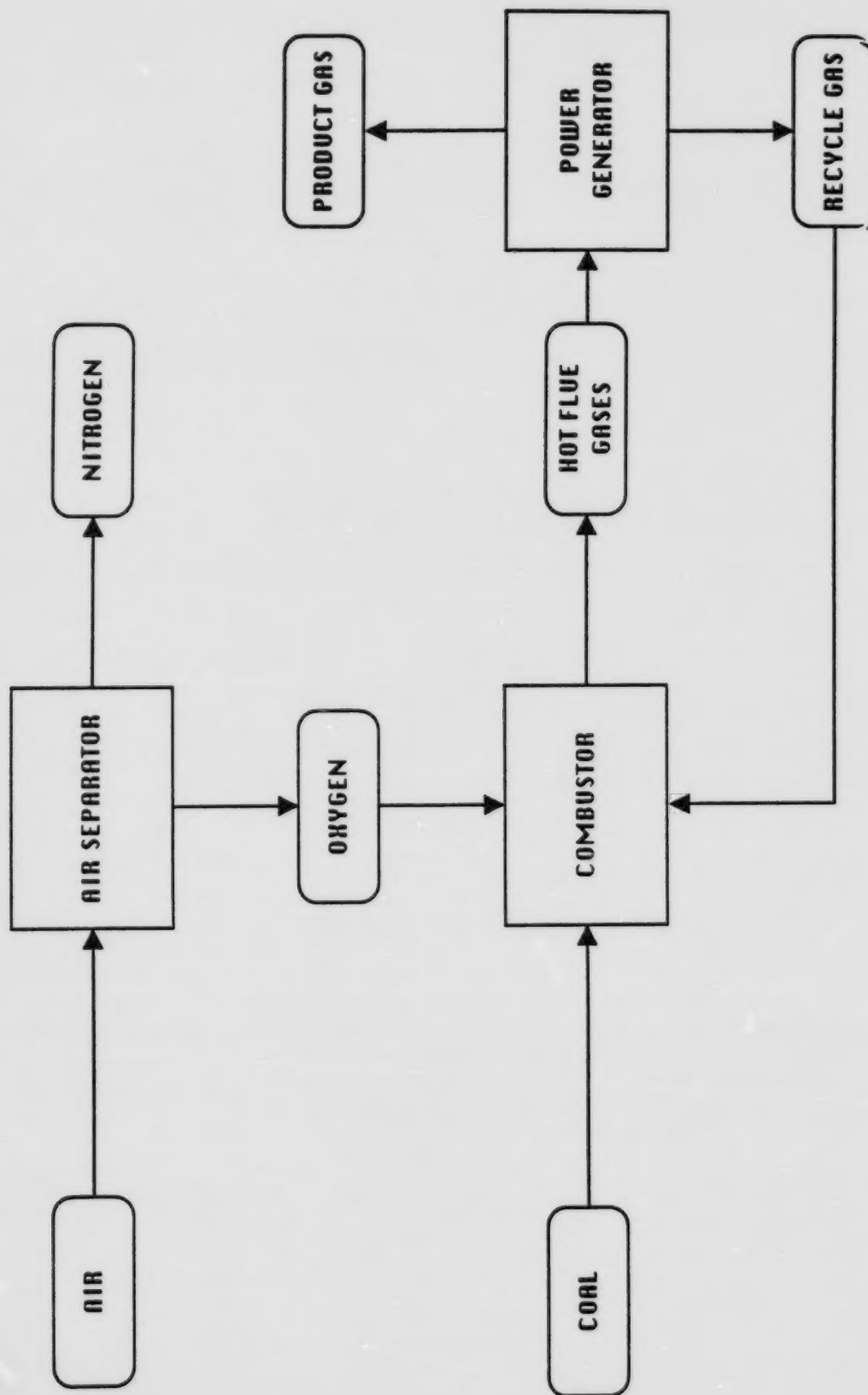


FIGURE 4. SCHEMATIC FLUE GAS RECYCLE COMBUSTION FLOWSHEET

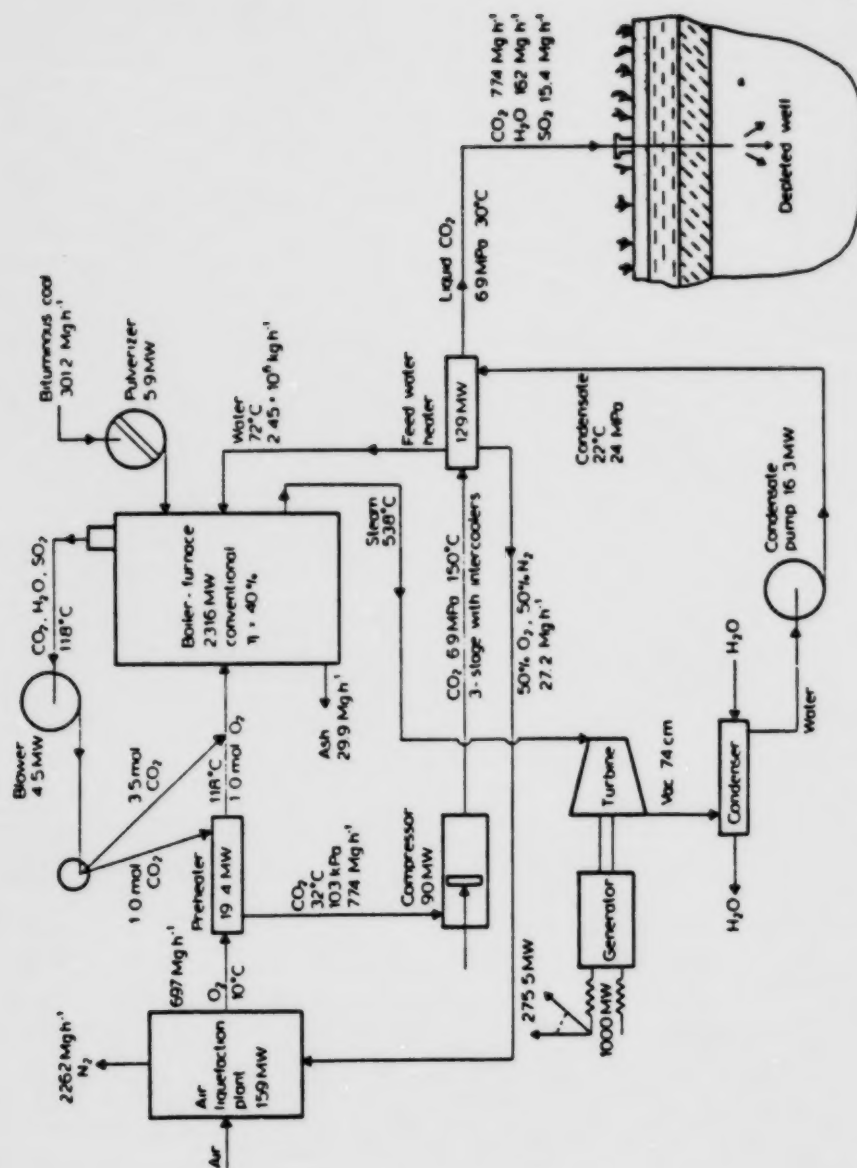


FIGURE 5. MORE DETAILED FLUE GAS RECYCLE COMBUSTION FLOWSHEET

Source: Fuel, Volume 61, May 1982.

Wolsky and his associates have summarized the economics of the process, as shown in Table 5. A comparative study of CO₂ recovery from the flue gas recycle process ("CO₂/O₂ process") with MEA scrubbing and from other alternatives was conducted recently; results are shown in Table 6. The conclusion of these estimates seems to be that the flue gas recycle process is attractive. Note that Intech did not include capital investment which is why their estimate is \$16/ton vs. about \$40/ton of carbon dioxide in the ANL calculation.

A key issue in assessment of the flue gas recycle process is the cost of oxygen because it represents about 80 percent of the costs. The relationship between oxygen plant capital cost and the design capacity is shown in Figure 6. There is not great improvement for scales larger than about 500 TPD and costs rise prohibitively below about 300 TPD.

Wolsky and coworkers have only counted on using air liquefaction for oxygen production. Improvements in alternatives could improve the position of this process. One such possible improvement that may be especially attractive in Western Canada is the Thermal Swing Absorption Oxygen process described in the New Topics section.

Wolsky (1990) reaches the conclusion that the lower the hydrogen content of a fuel, the better the prospects for the flue gas recycle process. The reasoning is that higher-hydrogen fuels produce less carbon dioxide per unit of oxygen consumed. In his scenario, which favors coal combustion, the carbon dioxide is sold for EOR usage. We also considered another scenario in which the carbon dioxide had to be stored at no value, after additional transportation and compression costs were incurred. In this scenario, the higher the hydrogen contents of the fuel the less carbon dioxide that has to be handled and the better the fuel.

Another important issue is whether the flue gas recycle process should be commercialized first for new steam and power plants or for retrofits. Battelle believes that for new power plants that exceed 300 MW the integrated gasification combined cycle approach appears better than the flue gas recycle approach. For smaller new facilities and for retrofits, the flue gas recycle process appears to have a potential niche. We therefore focused on the retrofit application for the flue gas recycle process technology where it has relatively minor competition.

TABLE 5. COST OF CO₂ BASED ON RECOVERY FROM A COAL-FIRED POWER PLANT: CO₂ RECOVERED = 500 TONS PER DAY

Component		Value, \$
Capital Costs		
O ₂ Plant		13.6 million
Recycle Piping		2.4 million
Total		16.0 million
Annualized (25% FCR) ^(a)		4.0 million per year
Annualized (15% FCR)		2.4 million per year
Per Ton of CO ₂ at 1 atm	<u>25% FCR</u>	<u>15% FCR</u>
80% CF	27.39	16.43
70% CF	31.30	18.78
Operating Costs (per ton CO ₂)		
Electricity		
\$0.05/kWh		13.13
\$0.01/kWh		2.62

(a) Fixed-charge-rate on capital, annualization factor.

Source: A.M. Wolsky, E.J. Daniels, and B.J. Jody, "Recovering CO₂ from Large- and Medium-Size Stationary Combustors", Argonne National Laboratory, for presentation at the 83rd Annual Meeting and Exhibition, Air & Waste Management Association, June 24-29, 1990.

TABLE 6. CARBON DIOXIDE-COLLECTION METHODS

	MEA		Coal		CO ₂ /O ₂ Process
	Base Case	Scrubbing	Gasification		
Plant net power, in MW	372.3	360.6	372.3		272.3
Plant efficiency, percent	33.4	20.1	27.8 ^(a)		24.9
Capacity factor, percent	65	65	65		65
Annual generation, MWh	2,119,876	2,053,256	2,119,876		1,575,450
Capital costs for CO ₂ removal, \$	--	320.8	154.7		265
Annual operating cost, \$	--	56.5	14.1		45.8
CO ₂ removed, ton/yr	--	2,105,026	2,306,131		2,221,554
CO ₂ to atmosphere, ton/yr	2,339,283	1,673,404	289,371		116,583 ^(b)
Annual Cost of CO ₂ Control					
\$/Ton removed	--	50	16		21
\$/Ton emissions decrease	--	177	21		28

(a) The Intech authors use 34.4 percent as the efficiency of the IGCC technology without capture of carbon dioxide. A more standard industry estimate is 38.7 percent (Blok, et al., 1989).

(b) This value is based upon the assumption that the plant will startup on air.

Source: Intech Inc., Coal & Synfuels Technology, Vol. 12, No. 10, March 11, 1991.

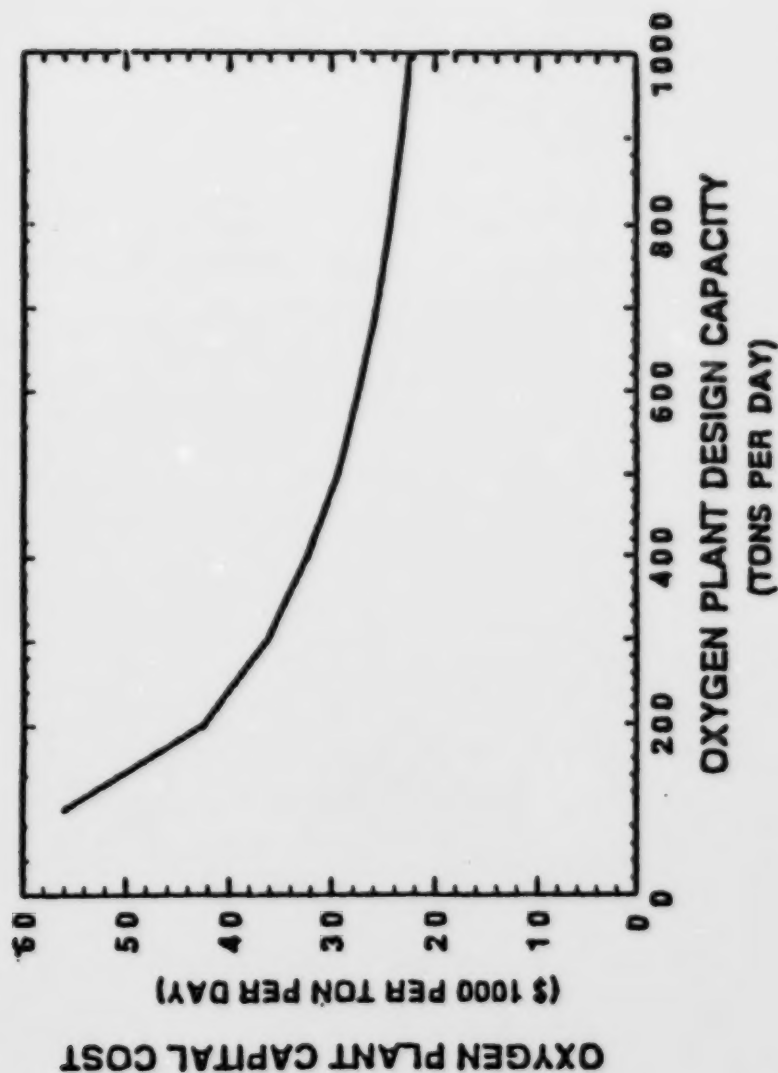


FIGURE 6. UNIT COSTS OF O_2 DECREASE WITH INCREASING PLANT SIZE

Source: A.M. Wolsky, E.J. Daniels, and B.J. Jody, "Recovering CO_2 from Large- and Medium-Size Stationary Combustors", Argonne National Laboratory, for presentation at the 83rd Annual Meeting and Exhibition of Air & Waste Management Association, June 24-29, 1990.

Battelle's team has engineers that are familiar with retrofitting boilers. They have raised the following issues:

- (1) Old boilers are leaky. When air leaks in, the product is diluted with nitrogen, making CO_2 recovery less attractive and, potentially increasing NO_x emissions.
- (2) Conversely, when carbon dioxide leaks out, it may represent a safety hazard; there is the possibility of suffocation in enclosed spaces.
- (3) Leaks in air preheaters and in bottom ash hoppers could cause as much as 20 percent of the carbon dioxide to be lost.
- (4) Carbon monoxide emissions are likely to be higher for O_2 - CO_2 combustion systems. Some evidence suggests CO emissions may increase in proportion to the CO_2 content of the flue gas; i.e., by a factor of 6.
- (5) There is a dilemma in wet recycle vs. dry recycle. Wet recycle is preferred from an energy production viewpoint in that the heat of vaporization of the water does not have to be rejected to the environment. Dry recycle is preferred for drying coal in the coal pulverizer. This might be resolved by taking a side stream to supply the pulverizer.
- (6) Some retrofit jobs may require installation of larger fans to overcome pressure drop in the recycle loop and to handle the different gas mixture.
- (7) Improved control will be required to avoid boiler explosions that may accompany fuel interruptions. Because CO_2 and O_2 are fed separately, a drop in the CO_2 feed rate will result in an increased level of O_2 .

Therefore, should a brief fuel interruption be accompanied by a reduced flow of O_2 , the restored fuel flow may confront an O_2 -rich atmosphere, leading to an explosion hazard. This problem can be handled by insisting on upgrading of controls when the retrofit is made.

None of these issues represent fatal flaws. The primary concern is that retrofitting implies less control over the plant environment in which the new technology is introduced. This situation could mean that the initial demonstration facility should be new, just so that retrofitting problems do not cause an unjust evaluation of the feasibility of the flue gas recycle process.

The path that Battelle suggests is to move toward retrofit if the initial flue gas recycle combustion facility is successful. However, it is possible to commercialize this technology by constructing new facilities that use pressurized combustors that use the flue gas recycle combustion concept. Despite its attractiveness in principle, the adoption of multiple innovations into one advanced system might cause "technology indigestion".

Capture Methods

If the avoidance strategy is not used, the carbon dioxide needs to be captured from the flue gas by some means. The exhaust gas can have many possible constituents and properties, depending on the combustion process that is used and on the selection of other emission controls. Figure 7 shows some of the significant constituents and properties. The partial pressure of carbon dioxide is important because such technologies as membranes perform best at high partial pressures while biomass has a relatively low upper limit on partial pressure. Gasification can give rise to hydrogen sulfide that is a competitive acid gas; conventional combustion yields oxides of sulfur. Sulfur oxides react with amines and deactivate them. Excess oxygen can interfere with amines. For such reasons as these, each combustion technology needs to be evaluated separately.

Figures 8, 9, and 10 provide an overview of the three primary means to capture carbon dioxide. They concern use of a change in physical state, mass transport,

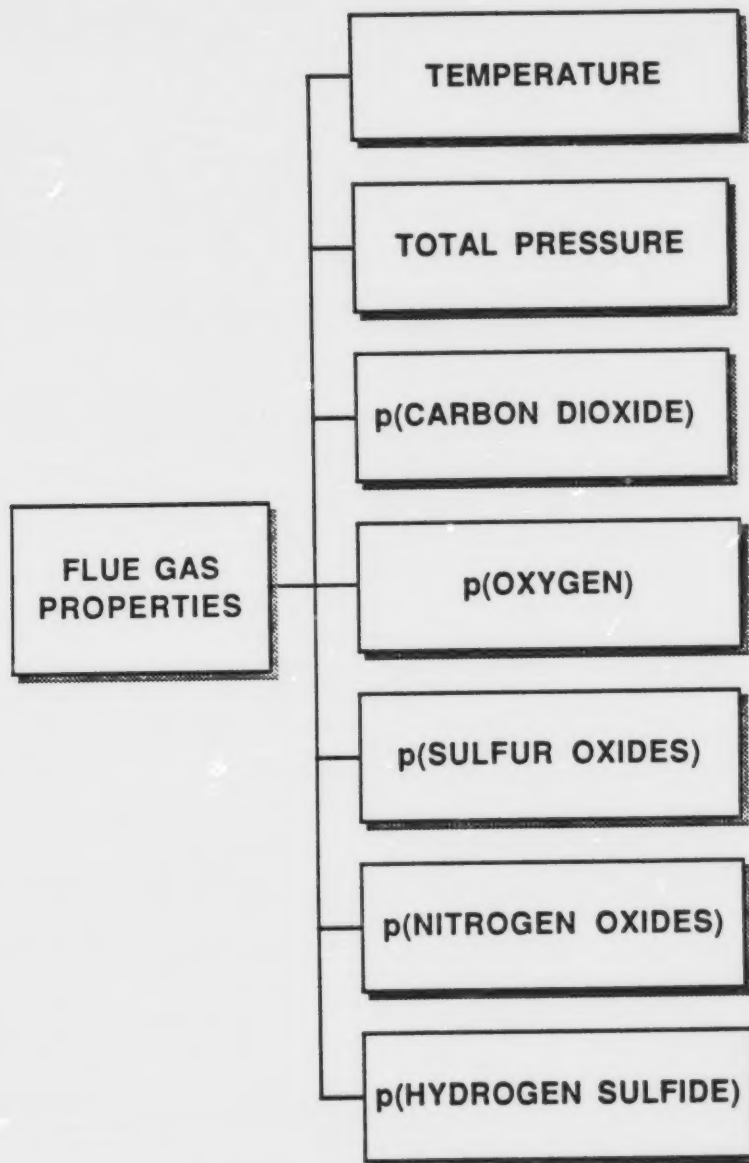
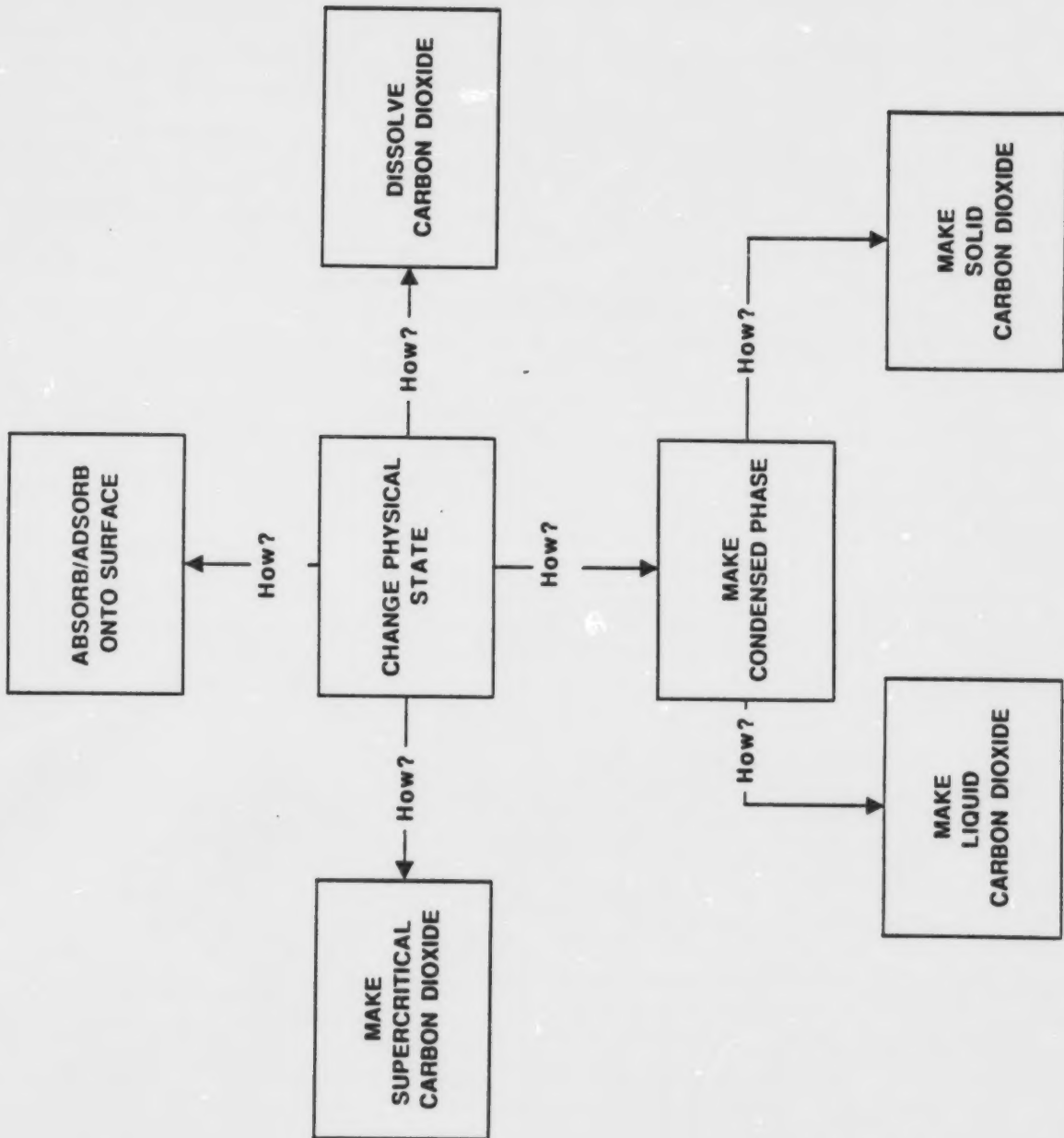


FIGURE 7. FLUE GAS PROPERTIES

FIGURE 8. CAPTURE CO₂ BY CHANGING PHYSICAL STATE

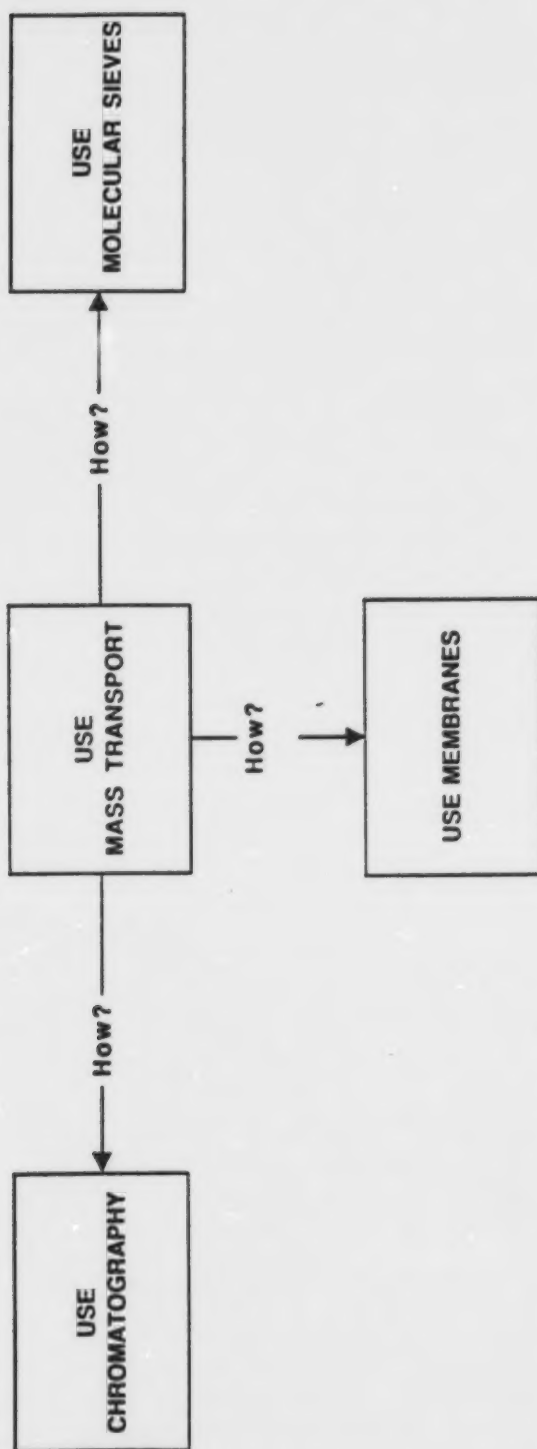
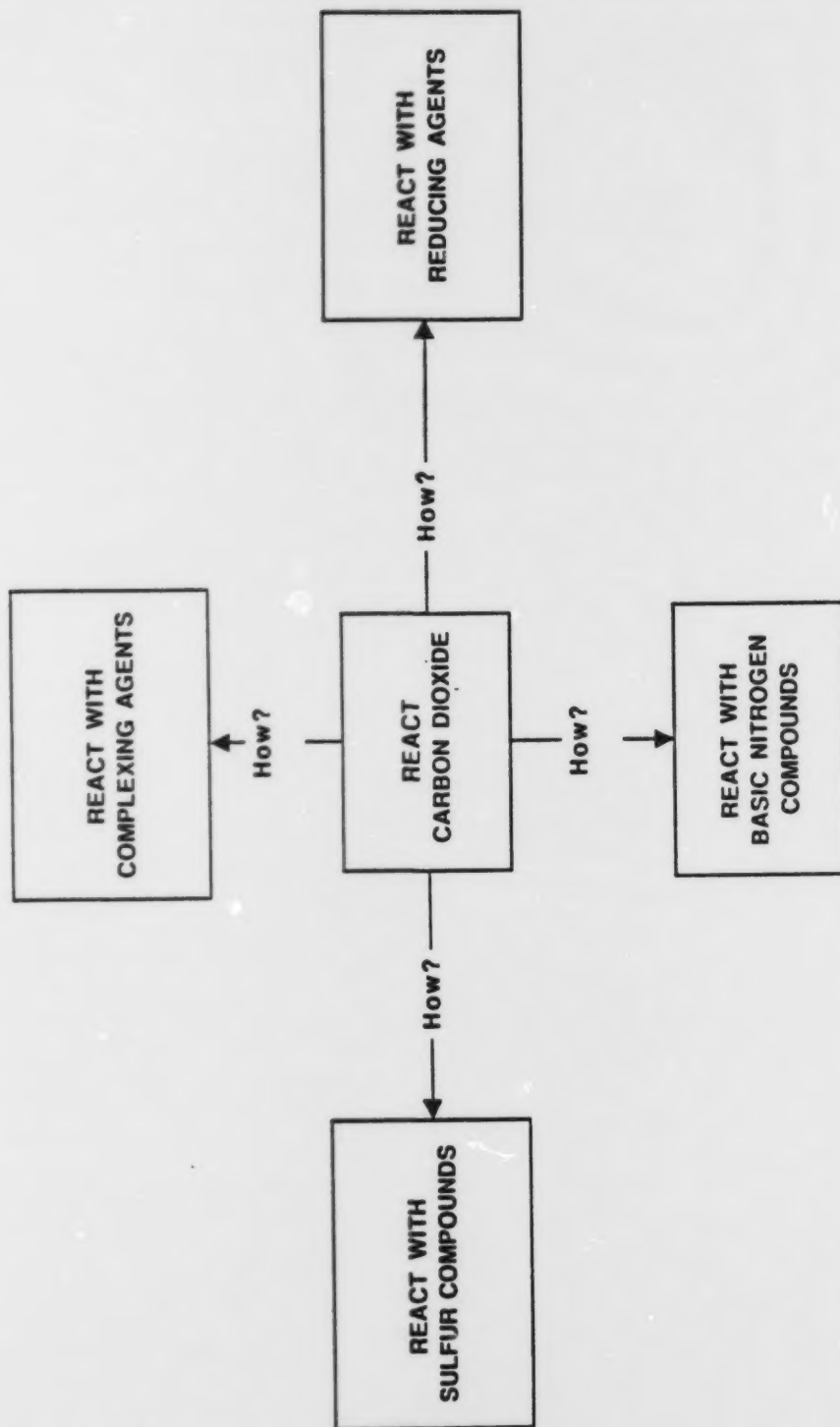
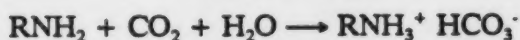


FIGURE 9. CAPTURE CO₂ BY USE OF MASS TRANSPORT

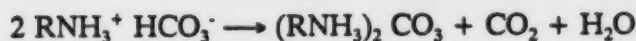
FIGURE 10. CAPTURE CO₂ BY CHEMICAL REACTION

and reaction, respectively. There is some overlap in these categories and common parlance interferes with accuracy. For example, amine absorption is really a set of chemical reactions.

Absorption Step:



Regeneration Steps:



There is research literature on dozens of carbon dioxide capture processes. The review in the Encyclopedia of Chemical Technology (Ballou, 1978) is a good starting point for investigating the state of the art in this area. However, our goal is a critical assessment of the serious contenders. They are treated in this section of the report. The alternatives that appear to merit further evaluation will be treated in the "New Topics" section.

Alkanolamine Absorption

The front-running amine absorption system is the Econamine® FG process that has been operated on a scale of 1100 TPD for recovering carbon dioxide from flue gas for use in EOR (Anada, 1983). Kerr McGee has used a different amine composition for many years at the 600 TPD scale. Based on information that is available to Battelle, the two processes are similar in that they use monoethanolamine (MEA) and differ with regard to proprietary additives that reduce oxygen corrosion. Other alkanolamines are used primarily when the objective is to capture hydrogen sulfide without capturing much carbon dioxide.

The Econamine FG process was developed by Dow and sold to Fluor Daniel. It is said to have the advantage that high concentrations of MEA can be used, thereby reducing energy costs and capital investment requirements.

This industry standard amine absorption system for use in grass roots and retrofit power plant applications has been evaluated by Fluor Daniel recently for Electric Power Research Institute (EPRI). The results are shown in Tables 7 and 8 for pulverized coal plants at the 500 MW scale. The cost basis is open to some discussion because a high sulfur coal is selected and the collected carbon dioxide is transported by pipeline 300 miles to the ocean, and transported an additional 100 miles where it is dumped at a depth of 1500 feet offshore. A more favorable case could be constructed with less transportation and a low sulfur coal; however, the key information in these tables is

- (1) Econamine FG and other chemicals that are associated with carbon dioxide capture cost about \$11 million per year, roughly doubling the cost of consumables.
- (2) Maintenance labor doubles. Most of the additional capital cost is in carbon dioxide compression which would be needed for any EOR process.

These estimates are by the supplier of the Econamine System!

The incremental plant costs for pulverized coal and GCC plants are compared in Table 9. The energy intensity of amine scrubbing is spot-lighted by the replacement power costs. The Intech study of power plants at about the 370 MW scale that was cited in Table 6 indicates that the use of MEA scrubbing reduces plant efficiency from 33.4 percent to 20.1 percent and costs more than twice what the flue gas recycle process costs per ton of carbon dioxide removed.

Some members of the Client Consortium have had pilot plant experience with MEA scrubbing; therefore, it is not necessary to belabor the fact that it is costly. However, it does get the job done if cost constraints are relaxed.

TABLE 7. CO₂ CAPTURE WITH AMINE SCRUBBING: TOTAL PC PLANT COSTS (JANUARY 1990, \$1000)

Plant Section	90% CO ₂ Removal					
	Base Case			Retrofit Case		
	Total Construc- tion Cost	Percent	Total Construc- tion Cost	Percent	Total Construc- tion Cost	Percent
Coal Receiving, Storage and Reclaiming	23,631 ^a	4.5	23,631	2.0	23,631	2.2
Steam Generation	92,695	17.6	92,695	7.9	92,695	8.7
Steam Turbine Generator System	84,019	15.9	153,527	13.2	84,860	8.0
Steam, BFW and Condensate System	18,529	3.5	18,529	1.6	18,529	1.7
Flue Gas Desulfurization System	139,302	26.5	141,736	12.1	113,707	10.7
CO ₂ Removal	--	--	169,059	14.5	169,059	15.8
CO ₂ Compression and Drying	--	--	61,424	5.3	61,424	5.8
Electrical	32,296	6.1	60,075	5.2	58,049	5.4
Instrumentation	24,115	4.6	24,115	2.1	24,115	2.3
Cooling Water System	22,653	4.3	26,679	2.3	26,582	2.5
Balance of Plant ^(a)	89,588	17.0	90,966	7.8	90,966	8.5
CO ₂ Pipeline	--	--	223,600	19.2	223,600	21.0
CO ₂ Disposal	--	--	79,200	6.8	79,200	7.4
Total	526,826	100.0	1,165,236	100.0	1,066,417	100.0
Contingency Allowance	52,683		116,524		106,642	
Total Plant Cost	579,511		1,281,760		1,173,059	
\$/kW ^(b)	1,129		3,830		3,469	

(a) Balance of plant consist of roads, paving, fencing, lighting, general buildings, fuel oil supply, auxiliary boiler, station build, firewater, chemical fire protection, plant and instrument air, raw water/make-up water system, underground piping, interconnecting pipeway, site preparation.

(b) Total plant cost divided by net power for the plant from the heat and material balance.

Source: S.C. Smelser and G.S. Booras, "An Engineering and Economic Evaluation of CO₂ Removal from Fossil Fuel-Fired Power Plants", Presented at 9th Annual EPRI Conference on Gasification Power Plants, Palo Alto, CA, October 17-19, 1990, published by EPRI.

TABLE 8. CO₂ CAPTURE WITH AMINE SCRUBBING: PC PLANT
ANNUAL OPERATING AND MAINTENANCE COSTS
(January 1990 Dollars in Thousands)

	Base Case	90% CO ₂ Removal	
		Retrofit Case	Grass Roots Case
Net Plant Output, MW	513.2	336.0	338.1
Operating and Maintenance Costs			
Operating Labor	2,978	3,504	3,504
Maintenance Labor	6,954	15,381	14,077
Maintenance Materials	10,431	23,072	21,115
Administrative and Support Labor	2,980	5,666	5,274
Total O&M Costs	23,343	47,622	43,970
Consumable Operating Costs ^(a)			
Raw Water	2,305	2,676	2,676
Catalysts and Chemicals	4,420	15,984	15,984
Ash/Sludge Disposal	6,754	4,599	4,599
Reclaimer Waste Disposal	0	2,029	2,029
Consumables at 100% Design Operation	13,478	25,288	25,288
Annual Fuel Cost at 100% Design Operation	55,895	55,895	55,895
Total Fixed Cost, \$/kW-yr ^(b)	29.6	92.1	84.5
Total Variable Cost, mills/kWh ^(b)	5.8	17.3	16.5
Fuel Cost, mills/kWh	12.4	19.0	18.9

(a) Variable costs and credits are based on operation at a 100% annual capacity factors.

(b) Calculated per EPRI TAG manual.

Source: S.C. Smelser and G.S. Booras, "An Engineering and Economic Evaluation of CO₂ Removal from Fossil Fuel-Fired Power Plants", Presented at 9th Annual EPRI Conference on Gasification Power Plants, Palo Alto, CA, October 17-19, 1990, published by EPRI.

TABLE 9. INCREMENTAL PLANT COSTS FOR
CO₂ RECOVERY

	\$/kW	
	Pulverized Coal ^(a)	GCC ^(b)
Steam Cycle Modifications	225	123
CO ₂ Removal	362	53
CO ₂ Compression	131	116
CO ₂ Pipeline and Disposal	649	754
Replacement Power	509	180
Total	1,876	1,226

(a) Amine Scrubbing.

(b) Selexol extraction of fuel gas before combustion.

Source: EPRI and Fluor Daniel.

Hindered Amines

Exxon has patented a series of hindered amines, some of which selectively remove hydrogen sulfide and reject carbon dioxide (Ho, et al., 1990). We will only consider those that are accelerators for removal of all acid gases (Say, et al, 1984). The hindered amines replace alkanolamines as promoters for the hot potassium carbonate process that has been used in over 400 commercial facilities. The benefits that have been demonstrated include about a 50 percent increase in acid gas removal capacity, compared with the conventional hot potassium carbonate operations.

The hindered amine concept is that conventional amines tend to form carbamates in which the carboxylate group is covalently bonded to the nitrogen of the amine. Hindered amines form ionic bicarbonate salts that can transfer carbon dioxide much more rapidly.

The state of the art hindered amines work best in the presence of hydrogen sulfide. In its absence, corrosion inhibitors are needed. Also, the preferred pressures are well above the atmospheric pressures that are involved in conventional boiler flue gases.

These amines may be more suited for use in integrated gasification combined cycle applications than in boiler applications. However, IGCC can use Selexol processing, apparently at low cost (Smelser and Booras, 1990).

Physical Solvents

Carbon dioxide is soluble in many solvents, especially polyethylene glycol dimethyl ether, tetrahydrothiophene dioxide, propylene carbonate, methyl pyrrolidone, and methanol. We will consider only three of these processes because they are of special interest. Those three are processes based on polyethylene glycol dimethyl ether, Sulfinol, and methanol.

Selexol Process. The Selexol solvent which is polyethylene glycol dimethyl ether (or a proprietary improvement on this solvent) is popular in evaluations of IGCC designs. In the EPRI IGCC design study, use of this physical solvent system under pressure resulted in minor increases in capital and operating costs, whereas the pulverized coal plants that had to use MEA were quite costly (Table 10 and 11). A simplified flowsheet for this separation process is shown in Figure 11.

Blok's estimate of the cost of electricity when MEA is used with coal vs. natural gas (Table 12) indicates that the efficiency loss is much greater for coal. The cost of desulfurizing coal flue gas plus the cost of MEA losses from residual sulfur in coal also exact a heavy penalty.

The Dutch developers of IGCC technology also use the Selexol system (Blok et al., 1989). Electricity costs are reduced about 25 percent and CO₂ costs less than half as much, when IGCC is used (Table 13).

They note that the present system leaves about 25 percent of the carbon dioxide in the absorbing fluid, after the desorption step. Although the system does remove all of the carbon dioxide ultimately, this situation does invite incremental improvement of the process.

Sulfinol Process. This family of solvents is based on tetrahydrothiophene dioxide, combined with various alkanolamines. Selection of the appropriate mixture can control the extraction to obtain mostly hydrogen sulfide. A second step with different amine ingredients can capture carbon dioxide. The general performance is similar to that of the Selexol extraction process and need not be pursued here, except to note that it also requires a relatively high pressure on the absorbing side. Thus, it is worthy of consideration for IGCC power plants that are operated in the shifted mode in which carbon monoxide is converted to carbon dioxide. However, conventional boilers cannot use this method now.

TABLE 10. TOTAL GCC PLANT COSTS (January 1990, \$1000 Except Where Noted)

Plant Section	Base Case		90% CO ₂ Removal	
	Total Construction Cost	Percent	Total Construction Cost	Percent
Coal Rec., Grinding and Slurry Preparation	34,154	5.5	34,707	3.4
Oxidant Feed	77,494	12.4	81,853	8.0
Gasification	69,588	11.2	74,123	7.2
Acid Gas Removal	34,724	5.6	55,080	5.4
Sulfur Recovery	19,832	3.2	22,048	2.2
Low Temperature Gas Cooling and Saturation	48,265	7.7	58,161	5.7
CO ₂ Compression and Drying	--	--	44,881	4.4
Combined Cycle Power Generation				
Gas Turbine Generators	79,038	12.7	79,038	7.7
Heat Recovery Steam Generation	33,509	5.4	32,744	3.2
Steam Turbine	29,143	4.7	28,200	2.8
General Facilities ^(a)	196,414	31.6	223,180	21.8
CO ₂ Pipeline	--	--	214,600	20.8
CO ₂ Disposal	--	--	76,000	7.4
Total				
Contingency Allowance	622,161	100.0	1,025,245	100.0
Total Base Plant Cost	68,438		117,217	
\$/kW ^(b)	690,599		1,142,462	
	1,600		3,015	

(a) General facilities consist of BFW treatment, roads, paving, fencing, lighting, general buildings, station buildings, fuel oil supply, natural gas supply, auxiliary boiler, demineralized water system, cooling water system, drains and blowdown, general waste water treatment, Texaco process water treatment, general makeup water, potable and utility water, environmental monitoring, firewater, chemical fire protection, plant and instrument air, electrical distribution, flare, barge unloading, interconnecting pipeway, communications, computer control and site preparation.

(b) Total plant cost divided by net power for the plant from the heat and material balance.

Source: S.C. Smelser and G.S. Booras, "An Engineering and Economic Evaluation of CO₂ Removal from Fossil Fuel-Fired Power Plants", Presented at 9th Annual EPRI Conference on Gasification Power Plants, Palo Alto, CA, October 17-19, 1990, published by EPRI.

TABLE 11. PC PLANT ANNUAL OPERATING AND MAINTENANCE COSTS
(January 1990 Dollars in Thousands)

	Base Case	90% CO ₂ Removal
Net Plant Output, MW	431.65	378.94
Operating and Maintenance Costs		
Operating Labor	6,833	7,008
Maintenance Labor	8,287	13,710
Maintenance Materials	12,431	20,564
Administrative and Support Labor	<u>4,536</u>	<u>6,215</u>
Total O&M Costs	32,087	47,497
Consumable Operating Costs ^(a)		
Raw Water	1,249	1,621
Catalysts and Chemicals	3,318	4,398
Ash/Sludge Disposal	2,738	2,986
By-Product Credit (Sulfur)	<u>(5,670)</u>	<u>(6,304)</u>
Consumables at 100% Design Operation ^(b)	1,635	2,701
Annual Fuel Cost at 100% Design Operation	46,288	50,480
Total Fixed Cost at 65% Stream Factor, \$/kW-yr ^(c)	48.32	81.47
Total Variable Cost at 65% Stream Factor, mills/kWh ^(c)	5.00	8.52
Fuel Cost, mills/kWh	12.2	15.2

(a) Variable costs and credits are based on operation at a 100% annual capacity factors.

(b) Consumables include by-product credit for sulfur.

(c) Calculated per EPRI TAG manual.

Source: S.C. Smelser and G.S. Booras, "An Engineering and Economic Evaluation of CO₂ Removal from Fossil Fuel-Fired Power Plants", Presented at 9th Annual EPRI Conference on Gasification Power Plants, Palo Alto, CA, October 17-19, 1990, published by EPRI.

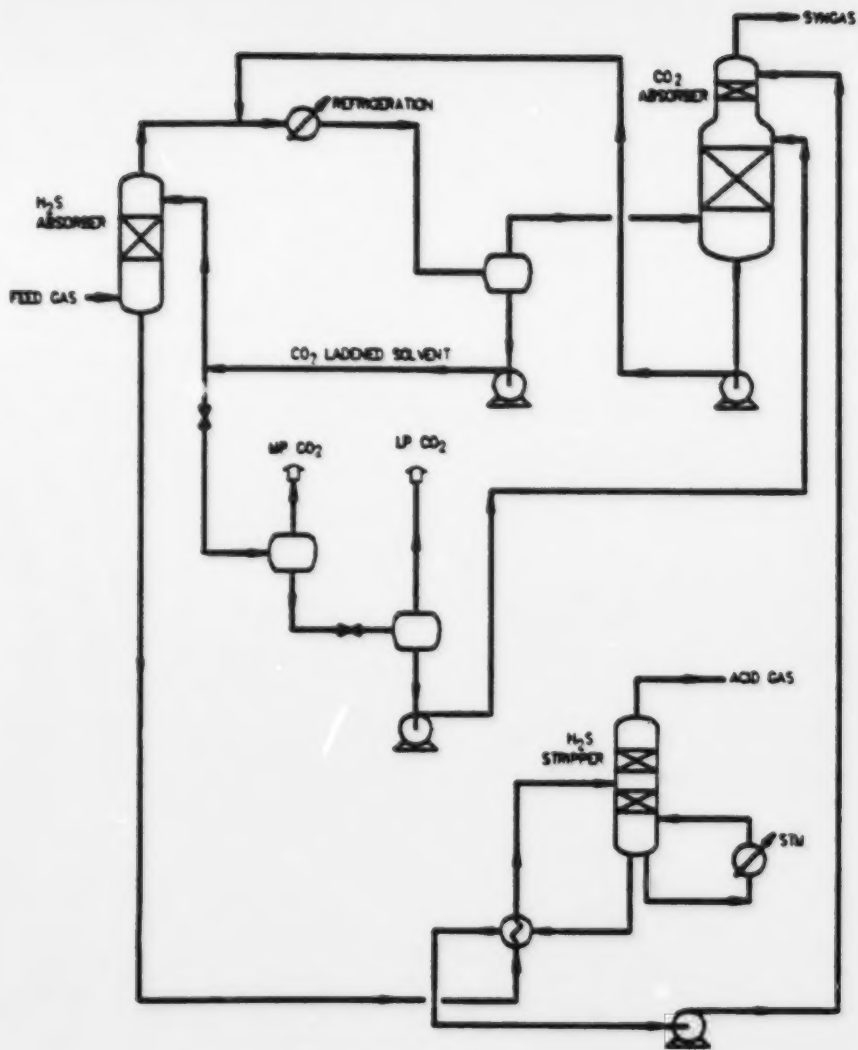


FIGURE 11. SIMPLIFIED SELEXOL FLOWSHEET

Source: S.C. Smelser and G.S. Booras, "An Engineering and Economic Evaluation of CO₂ Removal from Fossil Fuel-Fired Power Plants", Presented at 9th Annual EPRI Conference on Gasification Power Plants, Palo Alto, CA, October 17-19, 1990, published by EPRI.

TABLE 12. COMPARISON OF THE COSTS OF CARBON DIOXIDE RECOVERY FROM A COAL- AND A GAS-FIRED POWER PLANT

	Coal Plant		Natural Gas Plant	
	Without Recovery	With Recovery	Without Recovery	With Recovery
Fuel input, MW	1460	1460	1250	1250
Gross capacity, MW	600	600	600	600
Power loss by steam extraction, MW		-118		-60
Power demand control system, MW		-6		-3
Power demand for compression, MW		-42		-21
Net capacity, MW	600	434	600	515
Overall efficiency, LHV percent	41	29.7	48	41.2
Plant investment costs, Dfl ^(a) /kW	2000	2765	1250	1455
MEA-absorption unit, Dfl/kW		920		445
Compressor, Dfl/kW		690		340
Total investment costs, Dfl/kW	2000	4375	1250	2240
Plant O&M costs, Dfl/kW.year	74	100	30	35
Additional O&M costs, Dfl/kW.year		33		17
MEA purchase and recovery costs, Dfl/kW.year		41		21
Yearly exploitation at 6000 running hours				
Capital costs, min	77	122	48	74
O&M costs, min	44	77	18	34
Fuel costs, min	126	126	163	162
Electricity price, Dct/kWh	6.9	12.4	6.3	8.7

(a) One Dfl = \$0.45 (U.S.).

Source: Blok, et al., 1989.

TABLE 13. INCREMENTAL COSTS OF CARBON DIOXIDE RECOVERY FROM AN INTEGRATED GASIFICATION COMBINED-CYCLE PLANT

	Without Recovery	With Recovery
Fuel input, MW	1630	1630
Syngas production, MW	1316	1206
Syngas cooler steam production, MW	302	302
HRSG steam production, MW	352	321
Gross power	802	802
Gas turbine power, MW	480	440
Steam turbine power, MW	322	307
Internal power demand, MW	-92	-92
Power demand for compression, MW		-24
Net capacity, MW	710	631
Overall efficiency, LHV percent	43.6	38.7
Plant investment costs, Dfl ^(a) /kW	2200	2475
Shift reactor, absorption unit and compressor, Dfl/kW		550
Plant O&M costs, Dfl/kW.year	80	90
Additional O&M and chemicals, Dfl/kW.year		17
Yearly exploitation at 6000 running hours		
Capital costs, min	100	122
O&M costs, min	57	57
O&M for recovery, min		11
Fuel costs, min	141	141
Electricity price, Dct/kWh	7.0	8.7

(a) One Dfl = \$0.45 (U.S.).

Source: Blok, et al, 1989.

Methanol. Methanol is a good solvent for carbon dioxide, and the venerable Rectisol process was used for years successfully. Its Achilles Heel is that the absorber must operate at about 32 F (Ballou, 1978). The Alberta producer of methanol could redesign the process to permit the use of water that is chilled by Nature to greatly decrease the capital and operating costs of recovering carbon dioxide for disposal. When the weather is too warm, the system could be shut down. Alternatively, ice that is made during the cold season and stored for the warm season could be used to gain enough operating days per year to be acceptable..

Conclusions on Physical Solvents. The two physical solvents discussed here could be successful in the IGCC context. Probably propylene carbonate and NMP also could succeed because IGCC acid gas is a relatively easy substrate for processing.

The challenge is to develop physical solvent systems that can operate near atmospheric pressure with flue gases or to develop integrated processes that combine compression for carbon dioxide liquefaction and/or pipelining with a physical solvent separation process.

The methanol extraction process might make good use of the low temperature that prevails in parts of Canada much of the year. This is a special tactical advantage of Western Canada.

Cryogenic Separation

There is the opportunity to combine carbon dioxide capture with the next step in the disposal/utilization scenario, which is liquefaction. Kummel (1990) has described a system in which flue gas is cooled and pressurized to obtain liquid carbon dioxide and a cold, compressed gas stream that is used for cooling and for operating a turbine that recovers some energy as electricity.

This approach saves the capital investment in chemical recovery of carbon dioxide, but has high costs of pressurization. The opportunity to use this approach with technologies that use air liquefaction provides additional economies of the low temperature at which liquid nitrogen is obtained in air separation. This approach might compete

with the Selexol process in IGCC plants where the carbon dioxide is already under pressure and is at a relatively high percentage in the shift converter. It is a natural approach to prepare carbon dioxide for pipelining via the flue gas recycle process. Usage in situations in which the flue gas contains less than 18 percent (which is most boiler situations) appears to be less attractive.

A definitive thermodynamic study that is beyond the scope of this program would be needed to evaluate Kummel's suggestion to the point of substituting this approach for the currently chosen ones.

Membrane Technologies

This section presents some membrane system principles and their application to capture of carbon dioxide.

Membrane System Principles. A membrane system consists of four major aspects (Figure 12). The composition of the mixture to be separated is of greatest importance. There are easy mixtures and difficult ones so the desired combustion or gasification process should provide an easy mixture.

Gas separations depend on differences in the chemical affinity, size, and shape of the molecules to be separated. Carbon dioxide has a strong affinity for basic (alkaline) materials which can slow its permeation through a basic membrane. Small molecules can permeate rapidly; thus, kinetic diameter is an important consideration.

The mechanisms of permeation can be simple diffusion or transport systems that employ a carrier to help the permeating species move through the membrane (Figure 13). The membrane itself has a molecular structure that is tailored to facilitate the separation. If slow separations were acceptable, membranes would be highly successful. However, the more selective they are made, usually the slower they will perform.

The hardware configuration (Figure 14) involves especially the surface area of the membrane and provision for use of elevated pressure without damaging the

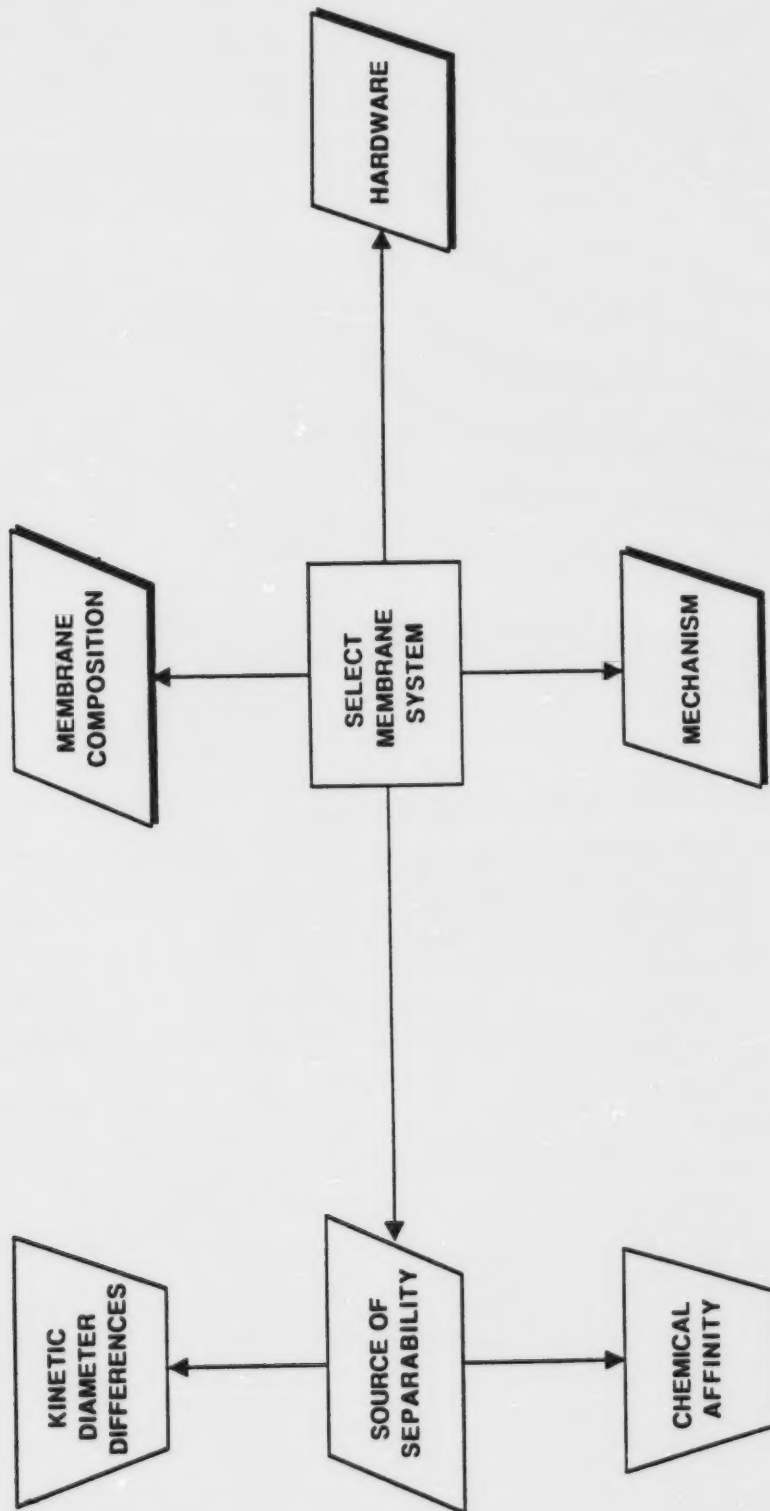


FIGURE 12. MEMBRANE SYSTEMS OPTIONS

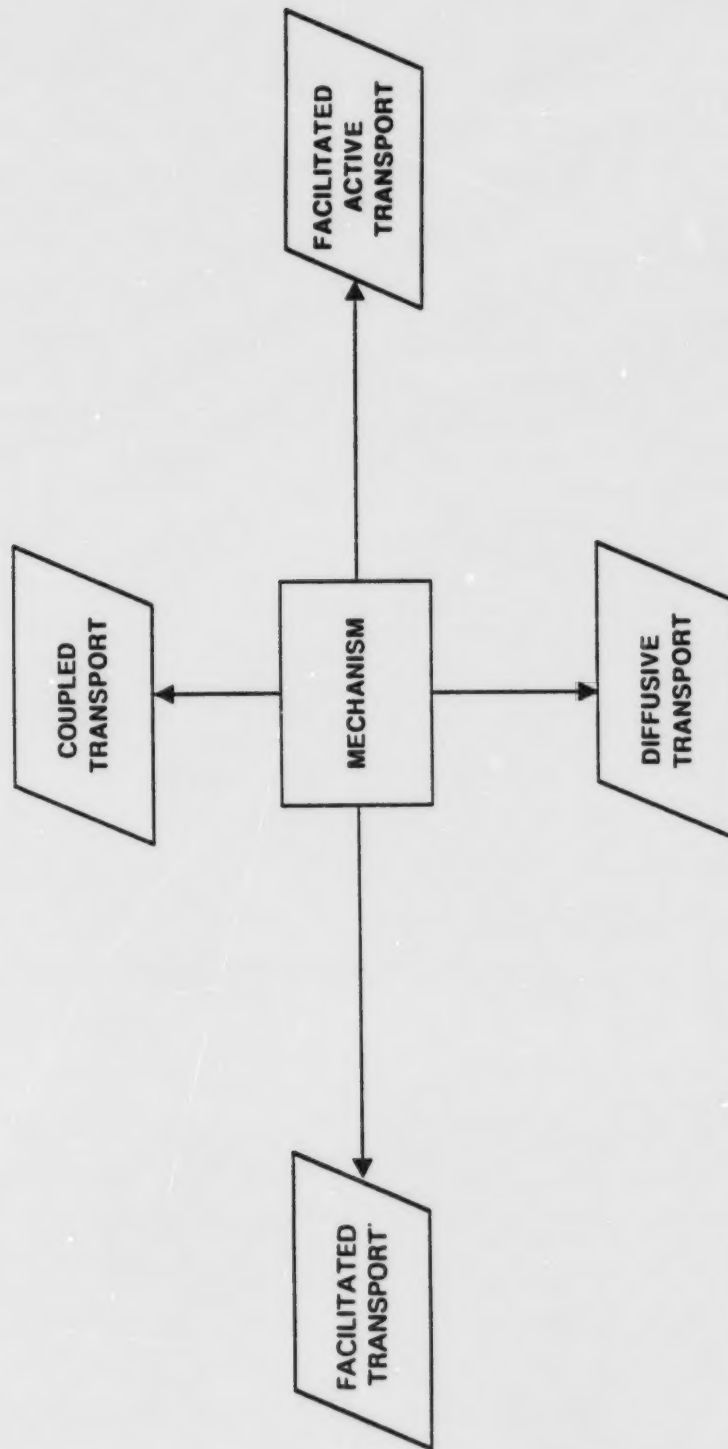


FIGURE 13. OPTIONS FOR MEMBRANE MECHANISMS

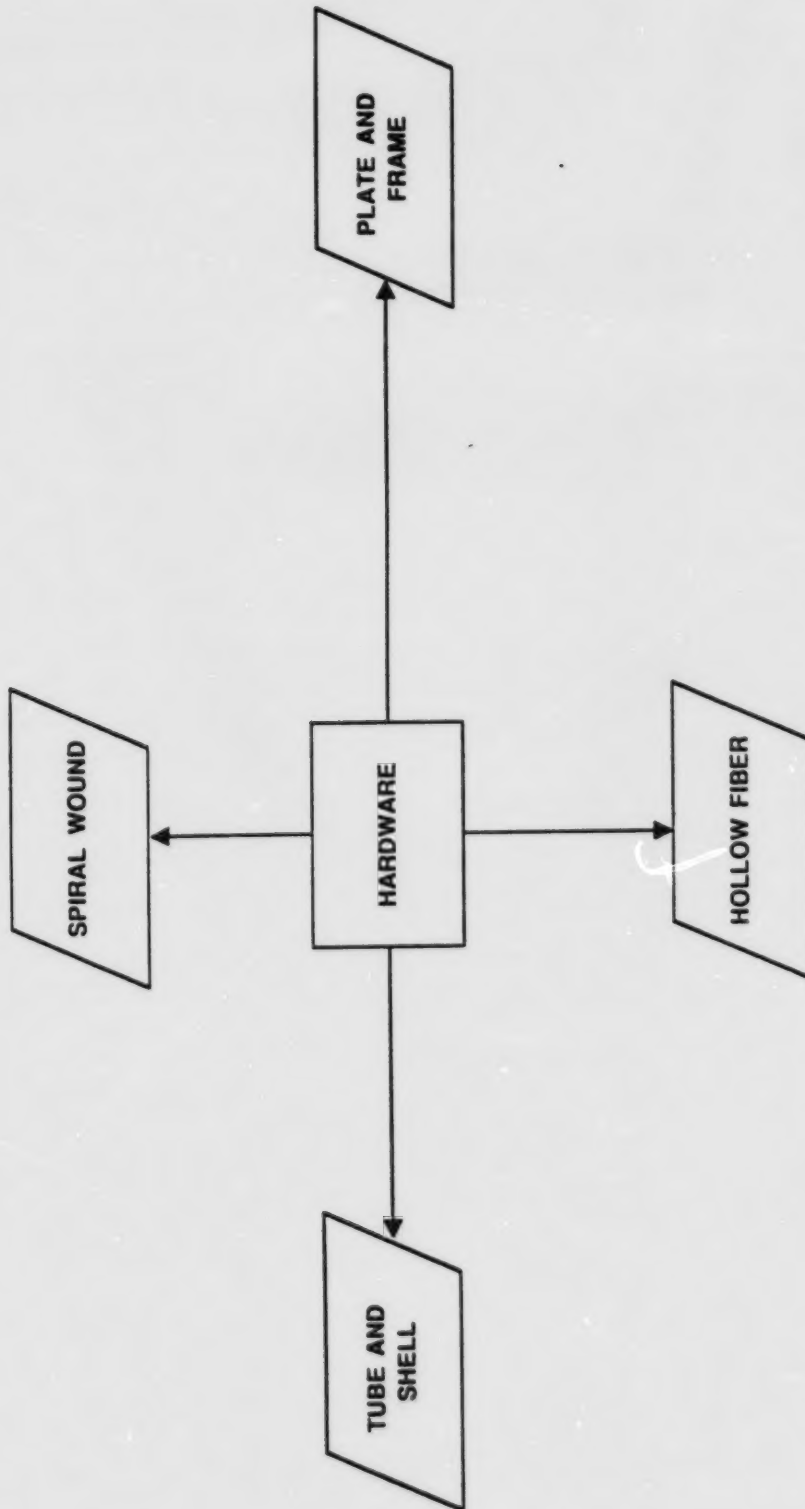


FIGURE 14. HARDWARE CONFIGURATIONS FOR MEMBRANE SYSTEMS

membrane. The more surface and the more pressure that can be applied, the faster the gas mixture can be separated. Hollow fiber membranes are especially favored for gas separations.

The composition of the membrane is the key to good separations. Polymers can be glassy or rubbery or both. The combination of the two types provides the basis for many gas separation membranes because one can optimize to get both speed and selectivity. The organic membranes are gaining competition from the inorganics and composites that are made from both types (Figure 15).

Application to Carbon Dioxide Separations. For recovery of carbon dioxide from stack gases, the most significant separation is carbon dioxide from nitrogen. The kinetic diameter of carbon dioxide is 0.05 nm less than that of nitrogen. Methane is a slow gas that tends to stay with nitrogen. Therefore, separation of carbon dioxide from these gases is relatively easy only when carbon dioxide is present in a high percentage, preferably well over 40 percent of the mixture and when relatively high pressures are available. Therefore, the use of membranes with conventional boilers is unlikely to develop.

In an IGCC power plant, it is desirable to separate hydrogen from carbon dioxide. In conventional applications at methanol plants, the membranes are selected to obtain both gases. For currently available Prism[®] type membrane separators, hydrogen tends to move with carbon dioxide because it is another fast gas. However, the differences in chemical reactivity of hydrogen and carbon dioxide indicate that this problem will be solved with the right membrane.

Compared with hydrogen, methane, and nitrogen, carbon dioxide is a reactive gas that can undergo facilitated or coupled transport through a membrane whereas hydrogen, methane, and nitrogen must use only diffusive mechanisms. The Gas Research Institute is developing a hybrid process that uses a tertiary amine/hollow fiber membrane combination to remove carbon dioxide from natural gas streams (GRI, 1990). In this case, the reactivity is exploited to slow down the diffusion of carbon dioxide.

Organic polymers are most selective as membranes when they are in either the glassy state or semicrystalline state. However, the rate of recovery of carbon dioxide

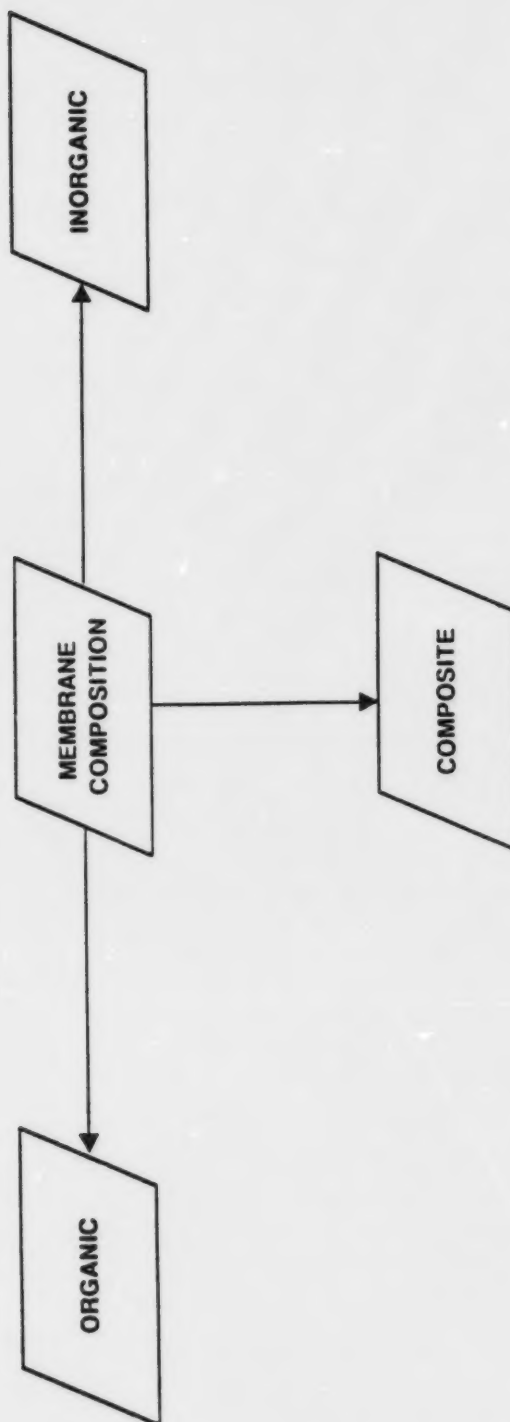


FIGURE 15. MEMBRANE COMPOSITION

is enhanced when the polymer is in the rubbery state (above the glass transition temperature). The result is a need to select or synthesize polymers with appropriate chain stiffness and interchain spacing for the combination of gases that are to be separated.

The prospects for ultimately replacing the Selexol process with a membrane process to separate hydrogen and carbon dioxide are excellent. These are indications that this replacement is a target of Japanese R&D.

Capture by Biomass

Although biomass may have a role to play in sustainable energy, the emphasis in this report is on its ability to capture carbon dioxide and to hold it for a significant period of time or allow its use to displace other resources that generate carbon dioxide in their production or use.

Photosynthesis is a light-catalyzed reduction of carbon dioxide that provides the basis for plant biomass and for a significant portion of microbial biomass. The potential availability of substantially greater quantities of carbon dioxide may pose global warming problems, but it also may provide the opportunity to manufacture more and better biomass for food, fuel, fiber, and other uses. Thus, intelligent use of carbon dioxide from stack gases and other emissions can improve the quality of life while decreasing the global warming threat.

The review by Fulkerson, et al in 1990 indicated that afforestation is the least costly method of controlling carbon dioxide emissions. It is convenient for those in the energy sector because there need not be a direct connection between the power plant and the tree or crop.

Western Canada's forestry and agricultural experts should be consulted regarding the suitability of intensive biomass plantations in this region. This author believes that short rotation forestry is unlikely to be suitable here. Also, the overall costs are much greater than they may seem when biomass production projects are conducted on a major scale. High yields are obtainable only on good soil, with adequate fertilization with N, P, and K. A field or forest stores biomass only as long as it does not rot or

catch fire or get converted into shopping centers. Composting releases carbon dioxide and thus is not a good move in managing biomass in the context of this study.

This discussion is confined to biomass situations in which a system is constructed that directly links the power plant with the biomass production unit.

Aquatic Biomass Systems. In 1982, Battelle completed a comprehensive study of microalgal aquatic biomass systems that could make use of brackish water. Even though the research is somewhat dated, we believe that the quotations from this report (provided as Appendix B) are helpful in providing the Consortium with an introduction to this area of technology.

When the aquatic biomass system (Figure 16) is viewed as a way to dispose of and use surplus carbon dioxide, certain points become evident:

- (1) Alkaline brines are desirable as the water resource because they form bicarbonate ions that can be utilized by some microalgal species. The bicarbonate does not lose carbon dioxide to the atmosphere as would happen with carbon dioxide dissolution in fresh water or acidic brines. It does not appear that the type of alkaline brines necessary for this application are present in Western Canada; however, this should be verified.
- (2) Areas with access to water that is already so saline as to be useless for other purposes would be preferred.
- (3) Construction of ponds and mechanical devices for transporting and introducing carbon dioxide and harvesting aquatic biomass is capital intensive. Revenues are needed to offset these costs. Choice of biomass that has substantial value as food, feed, fiber, or chemicals is the key to keeping net costs down.

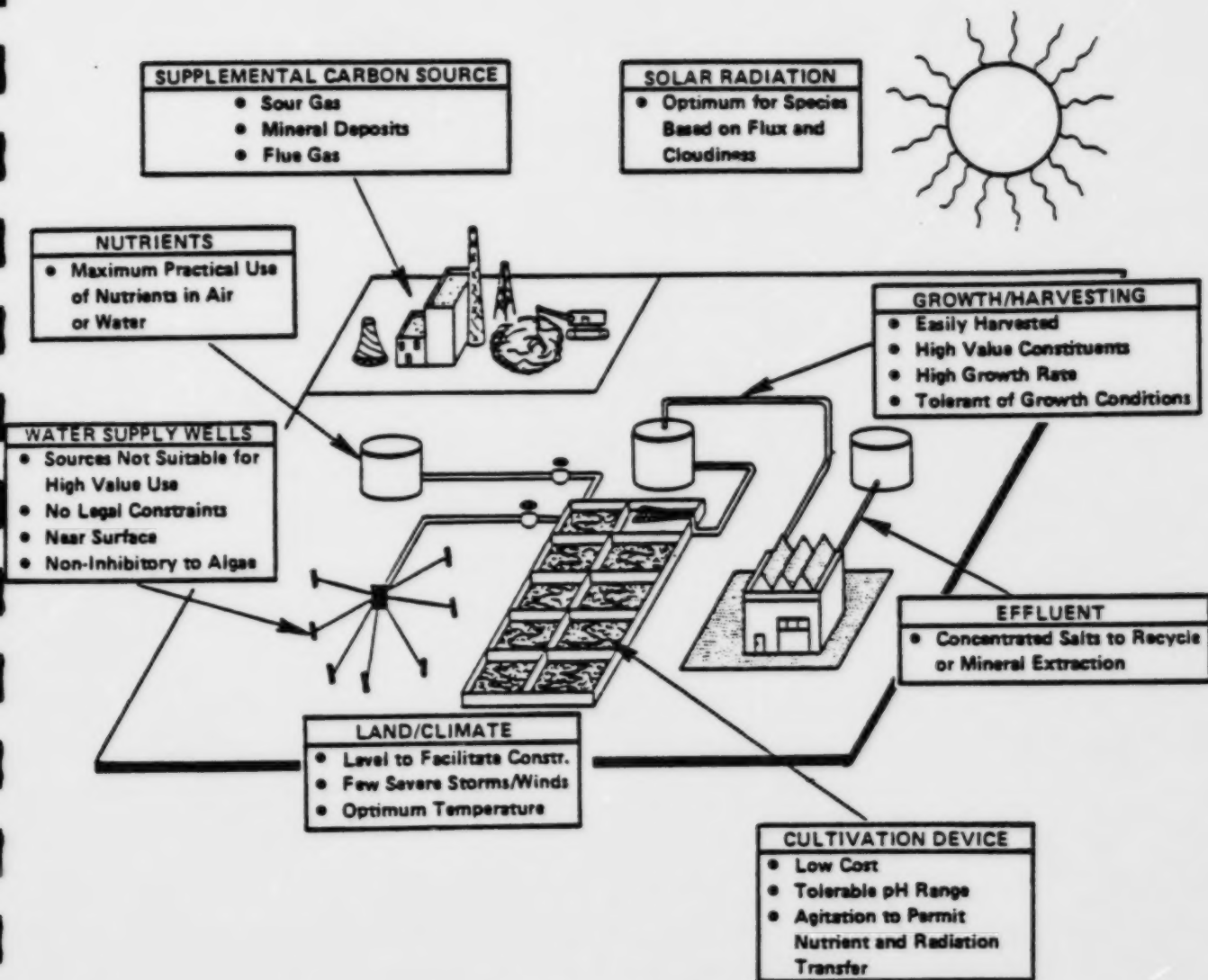


FIGURE 16. MICROALGAL BIOMASS SYSTEM

Source: B.W. Vigon, E.S. Lipinsky, et al, "Resource Assessment for Microalgal/Emergent Aquatic Biomass Systems in the Arid Southwest", Battelle's Final Report, December 23, 1982, to Solar Energy Research Institute, p 106.

- (4) Membrane technology can play a role in dispensing carbon dioxide to the ponds effectively as well as recovering the carbon dioxide from exhaust gas resources.

Sweet Sorghum Systems. In a major 5-year biomass program for the U.S. Department of Energy, Battelle developed a sugar crop that could be grown over a wide range of climatic and soil conditions. Sweet sorghum varieties that could grow as fast or faster than maize were grown in North Dakota and in Ontario. Other varieties grew in Texas.

This crop formed the basis for a system (Figure 17) that could produce electricity and chemicals, oxygenated fuels, or fiber products. Our system provides a storable sugar concentrate that is suitable for fermentation. The residual biomass, after removal of the fermentable sugars, can be stored until needed by the power plant. A compressed biomass pile is constructed for this purpose. It is similar to a coal pile. Coal piles and sweet sorghum piles are stabilized by compression to exclude air and to retard oxidation. The mechanism with the sweet sorghum piles appears to involve control of the microbial environment so that many species of organisms are inhibited by the acid generating species, yet full degradation to methane and carbon dioxide which would be disadvantageous is also inhibited. This approach has been patented by Gunnerman and Farone (1986). The coolness of Canadian winters should increase the efficacy of the storage method.

The residual biomass is used as fuel for production of steam. The sugars are directly fermentable to ethanol, lactic acid, or other biomass chemicals/fuels. The carbon dioxide could be recovered from the flue gases formed by combustion of this very low sulfur fuel. The carbon dioxide could be used for enhanced oil recovery in appropriate geographical areas. During the growing season, the carbon dioxide might be used to enhance the yield of sweet sorghum. The potash in the biomass ash can be returned to the fields.

Sorghums have a wide geographical range, so that the coolness of much of western Canada is not necessarily a fatal flaw. For example, this crop can grow in parts

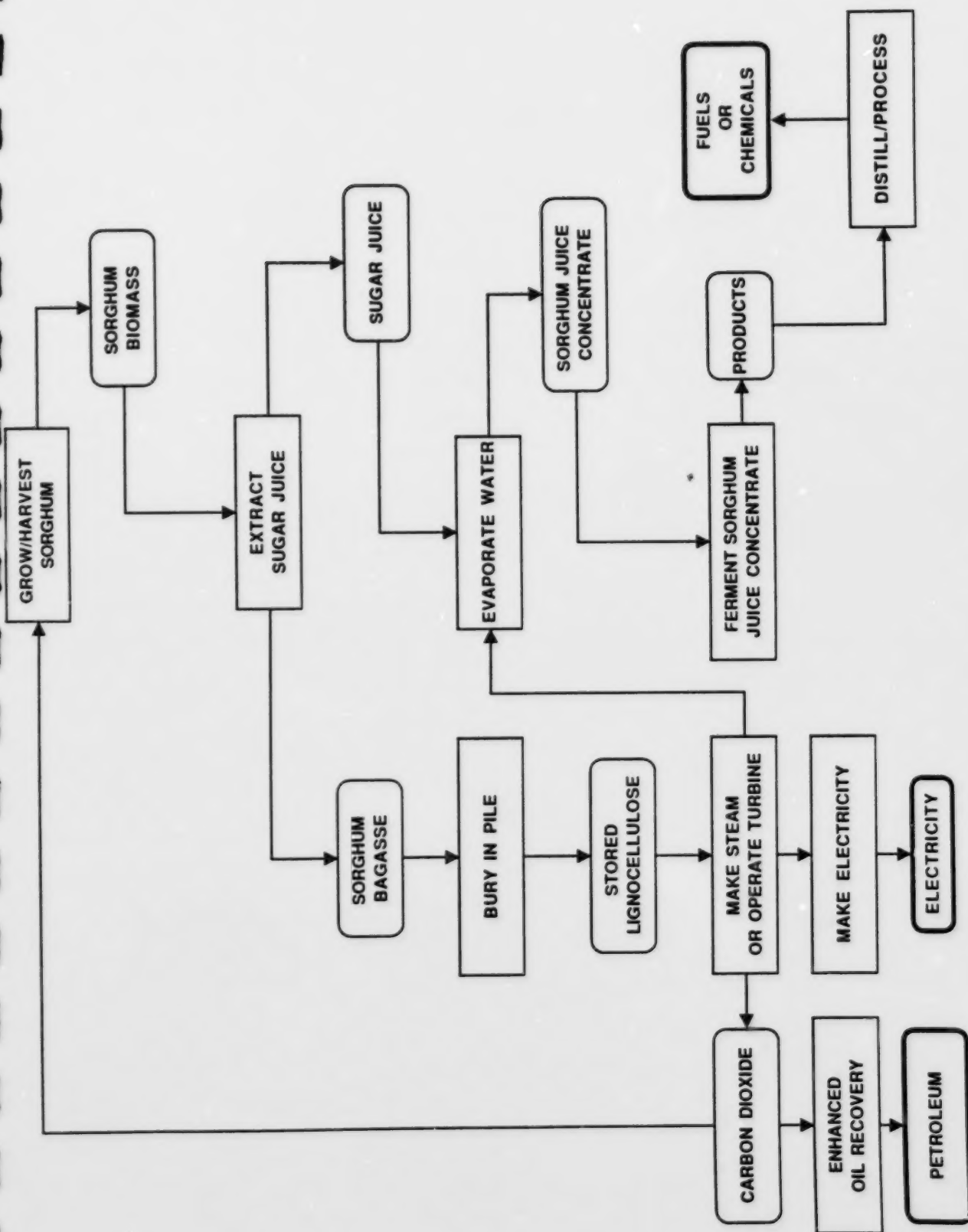


FIGURE 17. SWEET SORGHUM SYSTEM

of Scandinavia. We have observed good yields in Ontario. However, the crop is a short season one in northern latitudes. Battelle's evaluation of this concept indicated that it has some merits in places like California in which State agencies mandate the use of "green" technologies. We found in our pilot biomass tests that the best results were obtained with very high quality irrigated land with high solar insolation. Large applications of fertilizers and pesticides were needed to obtain the target yields.

Additional Biomass Insights. There are some additional insights that we believe are important to consider in evaluating whether to embark on biomass ventures involving carbon dioxide.

- (1) Carbon dioxide helps to conserve water in arid land situations, while also promoting higher biomass yields. When the stoma of plants are open to receive carbon dioxide, they leak water vapor. Higher carbon dioxide levels allow the stoma to stay closed a greater percentage of the time, conserving water.
- (2) Dr. D.O. Hall, of University College London, has found that many estimates of biomass yields are low because the extensive underground growth of roots is not considered. For some species, the underground, uncounted yield may equal the above ground growth. Underground growths of 25 percent of above ground growth are quite frequent.

Carbon Dioxide Disposal

Disposal options are shown in Figures 18 to 22. The critical assessments that relate to utilization are deferred to that section of this report. This section will be concerned primarily with the large scale use of Western Canadian brines. Other disposal issues will be covered in the New Topics section.

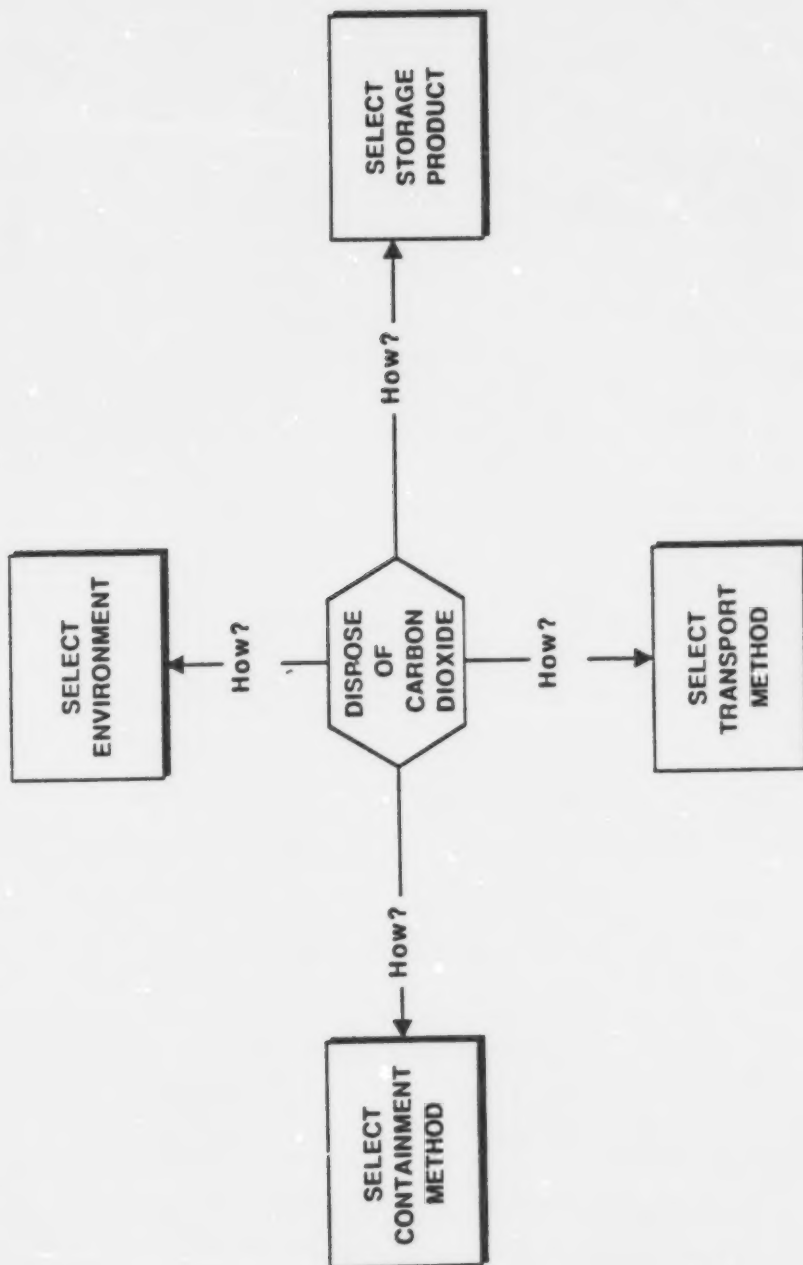


FIGURE 18. OPTIONS FOR DISPOSING OF CARBON DIOXIDE

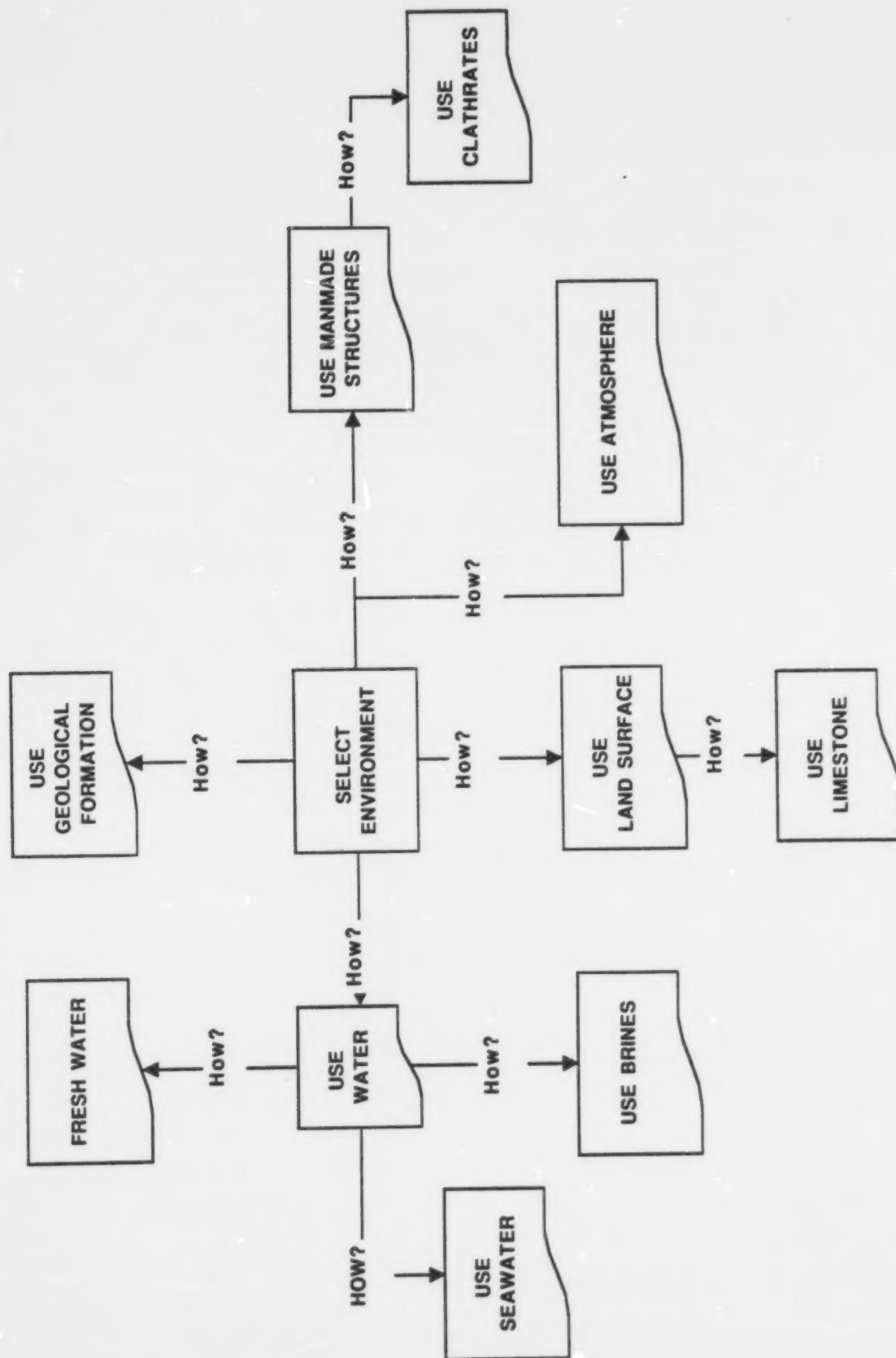


FIGURE 19. ENVIRONMENTAL OPTIONS

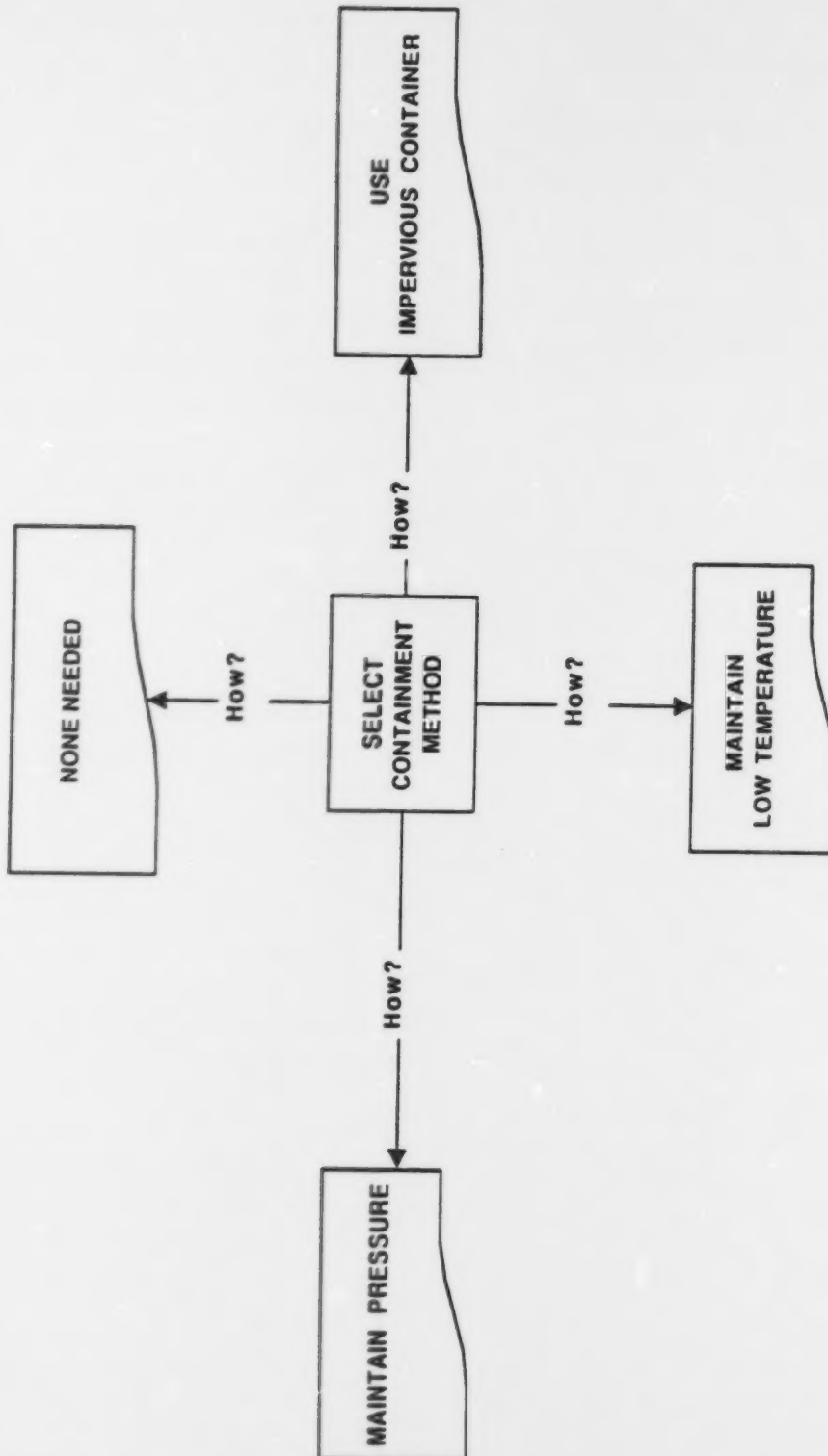


FIGURE 20. CONTAINMENT METHOD OPTIONS

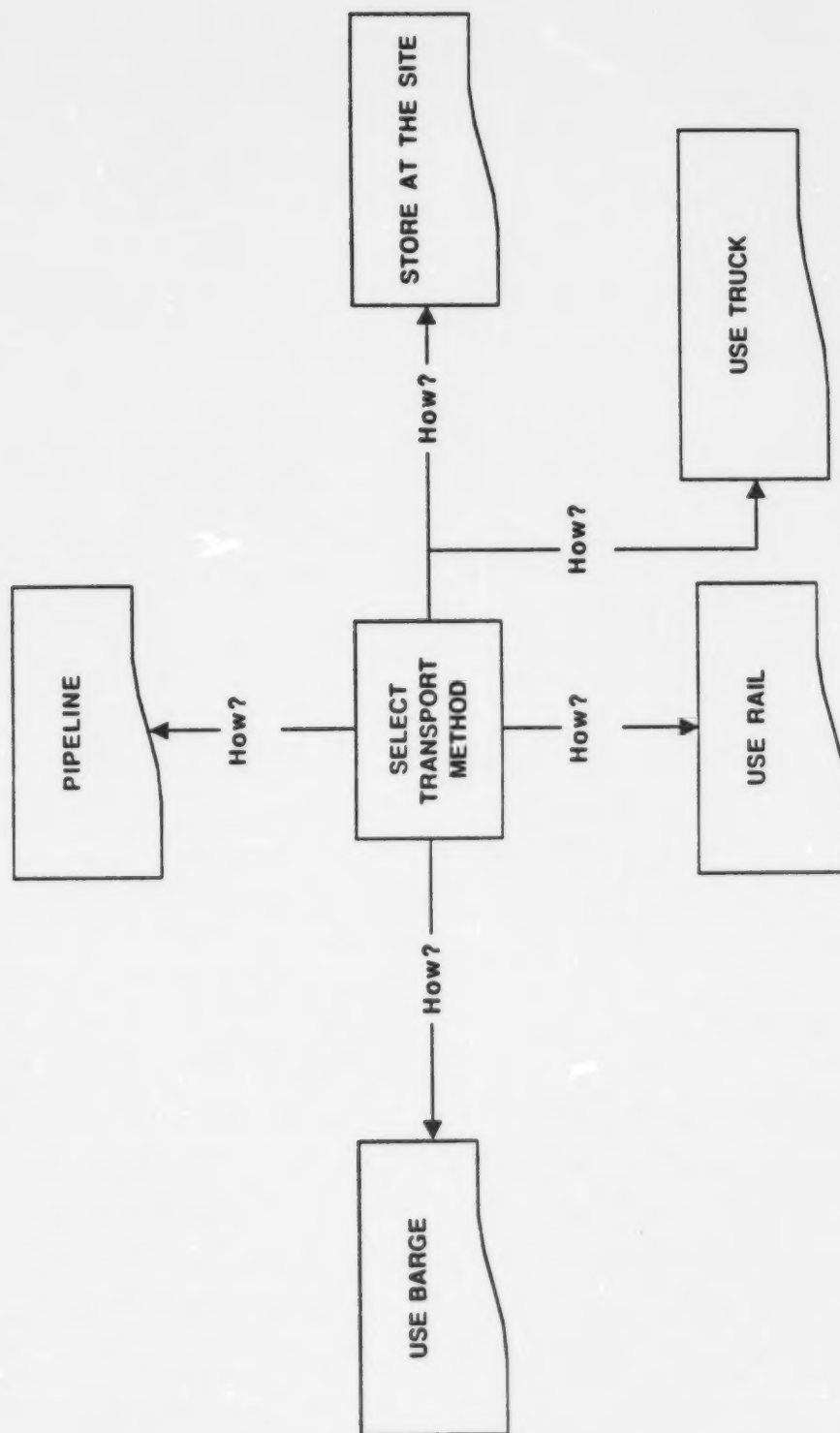


FIGURE 21. TRANSPORT METHOD OPTIONS

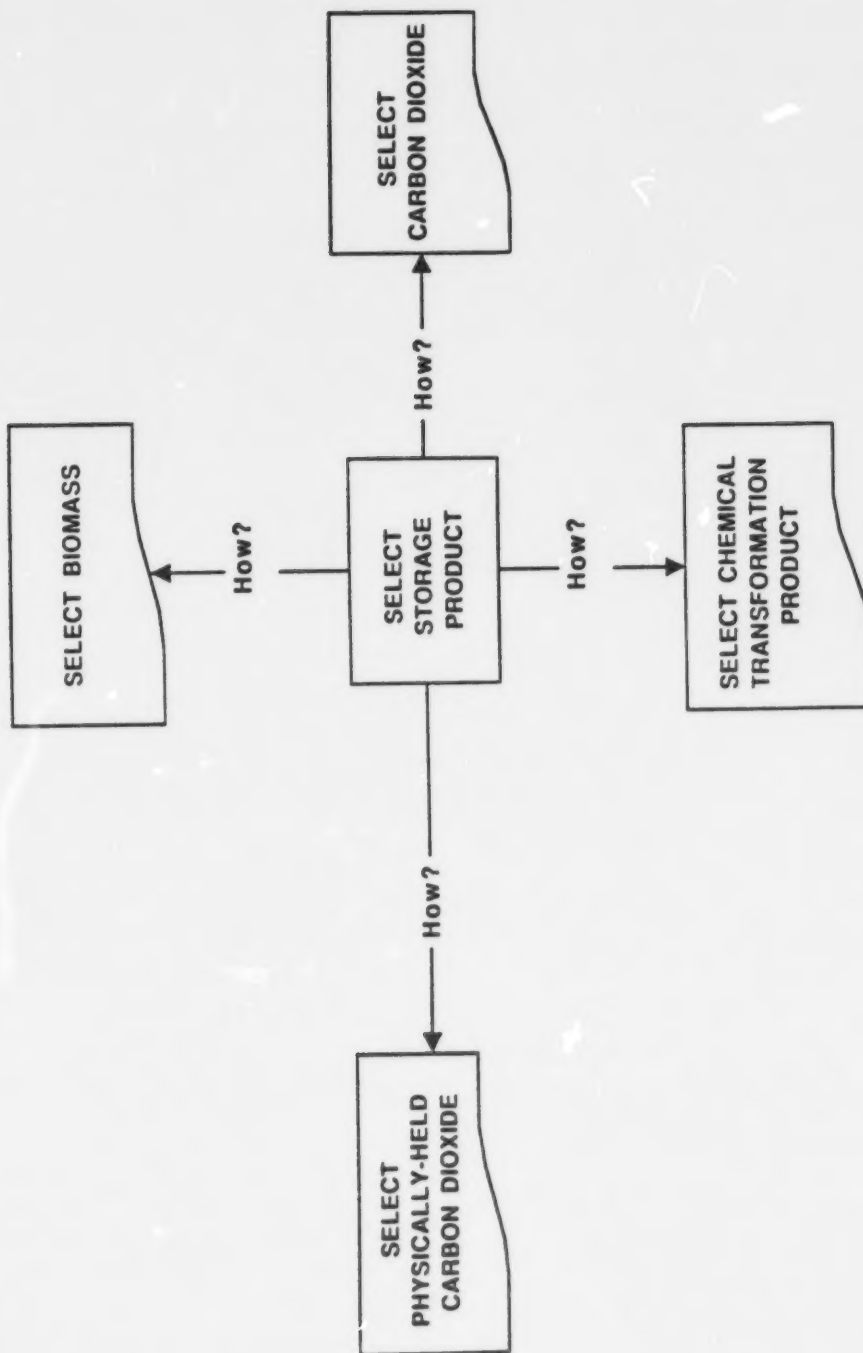
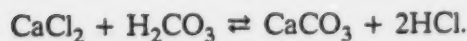
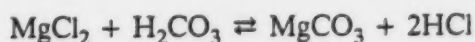


FIGURE 22. STORAGE PRODUCT OPTIONS

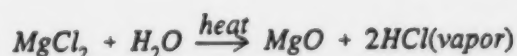
Disposal of Carbon Dioxide in Brines

Saskatchewan has some unique magnesium and calcium brines that might be used to sequester carbon dioxide. The concept has been published by Dr. Dunsmore (1990) and a working group has been evaluating the idea.

The relevance of this concept to this study is illustrated by Figure 23 that shows where the Elk Point Basin lies in Western Canada. Typical brine analyses are shown in Table 14. The problem is to cause the following reactions to go to the right when the equilibrium is surely far to the left:



The situation might be improved by using a time-honored way to make magnesium oxide from magnesium chloride which is high temperature reaction of water with magnesium chloride.



The reaction is driven to the right by departure of HCl gas from the scene of the reaction. The HCl is collected for sale or separate storage. The magnesium oxide should react very well with carbon dioxide.

It is not clear whether the decomposition of calcium chloride to the oxide and HCl gas goes very far toward completion. Experiments conducted at Battelle on the calcium chloride system indicates that it is not highly feasible. It would be better to start with magnesium chloride for which there are considerable data.

An alternative would be to attempt to make magnesium bicarbonate by reaction of a stream of carbon dioxide gas with the magnesium chloride-rich brine. The HCl gas would be entrained in the carbon dioxide stream and collected as an aqueous solution.

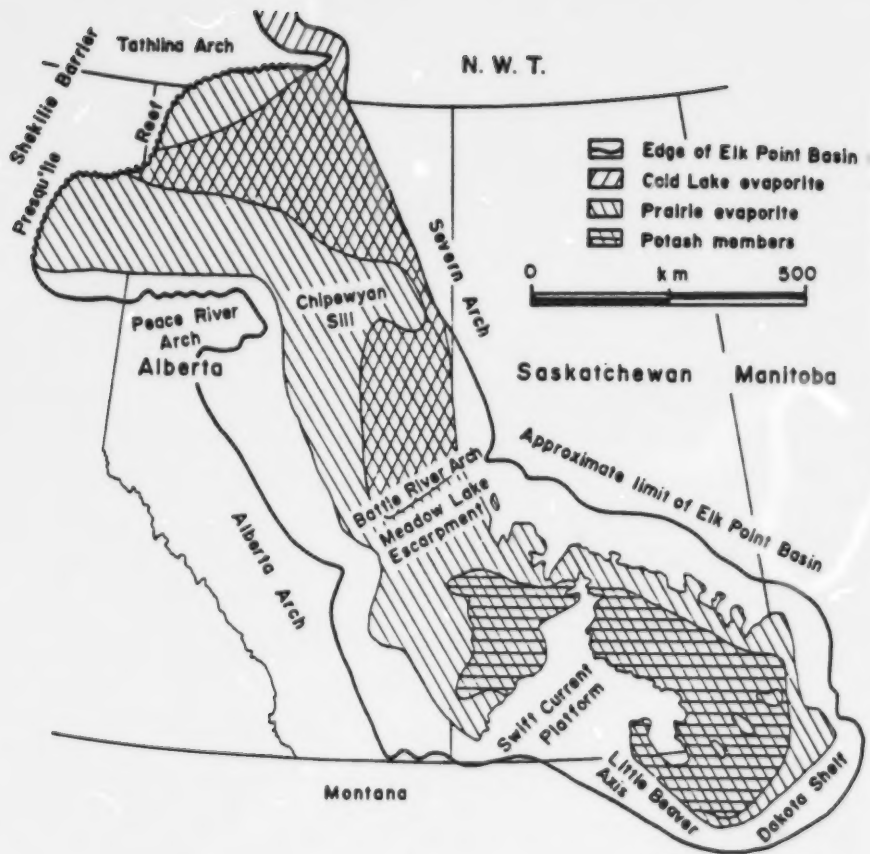


FIGURE 23. ELK POINT BASIN BRINE DEPOSITS

Source: Peter Sonnenfeld, Brines and Evaporites, Academic Press, Inc. p 403, 1984.

TABLE 14. COMPOSITION OF SASKATCHEWAN BRINES

	Ca-I	Mg-I	MG-II
Cl ⁻	335,000 mg/L	305,000 mg/L	302,000 mg/L
Ca ⁺⁺	135,000 ^(a)	7,500	25,500 ^(a)
Mg ⁺⁺	23,000	87,000 ^(a)	78,000 ^(a)
K ⁺	20,500	20,000	20,000
Na ⁺	6,200	10,350	9,400
Sr ⁺⁺	4,700 ^(a)	190	670
Li ⁺	21 ^(a)	3	14
Br ⁻	5,410 ^(a)	1,980	2,330
I ⁻	95 ^(a)	3	11
B	200 ^(a)	12	170
B ¹⁰ /B ¹¹	4.115	4.023	4.161
S.G.	1.3525	1.2670	1.2790

(a) Potentially commercial.

Source: Presented by H.E. Dunsmore, Geological Survey of Canada, at Federal/Provincial Industrial Minerals Meeting, Ottawa, Canada, October 18-19, 1990.

Deep Ocean Disposal

The surface of the ocean is saturated with carbon dioxide, but the depths have little or no carbon dioxide. A popular suggestion (Steinberg, 1984) is to pipeline liquid carbon dioxide out to 100 miles offshore and bury it at 1500 feet (Figure 24). An alternative is to drop dry ice overboard and let its density carry it to great depths in the ocean.

The Client Consortium has no British Columbia members; therefore, there is not intense interest in this concept for this report. However, such suggestions are likely to intensify the controversial nature of this disposal issue. There is some evidence that the high pressure could cause the carbon dioxide to form a clathrate (inclusion compound) in which about six molecules of water surround one molecule of carbon dioxide to yield a solid that is more dense than seawater. Because of this solid, the carbon dioxide might not disperse in an infinite ocean and might build up highly localized deposits instead. Experiments are said to be underway at the University of California at Santa Barbara to obtain more information on the environmental behavior of the clathrates of carbon dioxide.

Underground Storage

The Client Consortium is highly aware of the costs and technical aspects of using gas and oil wells to store carbon dioxide. When properly selected, these underground geological formations are quite gas tight.

Salt caverns have been suggested by Steinberg (1984); however, the saline solution that is produced during the mining operations would constitute an environmental problem.

Utilization Opportunities

Utilization routes require markets, products, and conversion processes to manufacture the marketable products from carbon dioxide. The markets that appear attractive for carbon dioxide are shown in Figure 25.

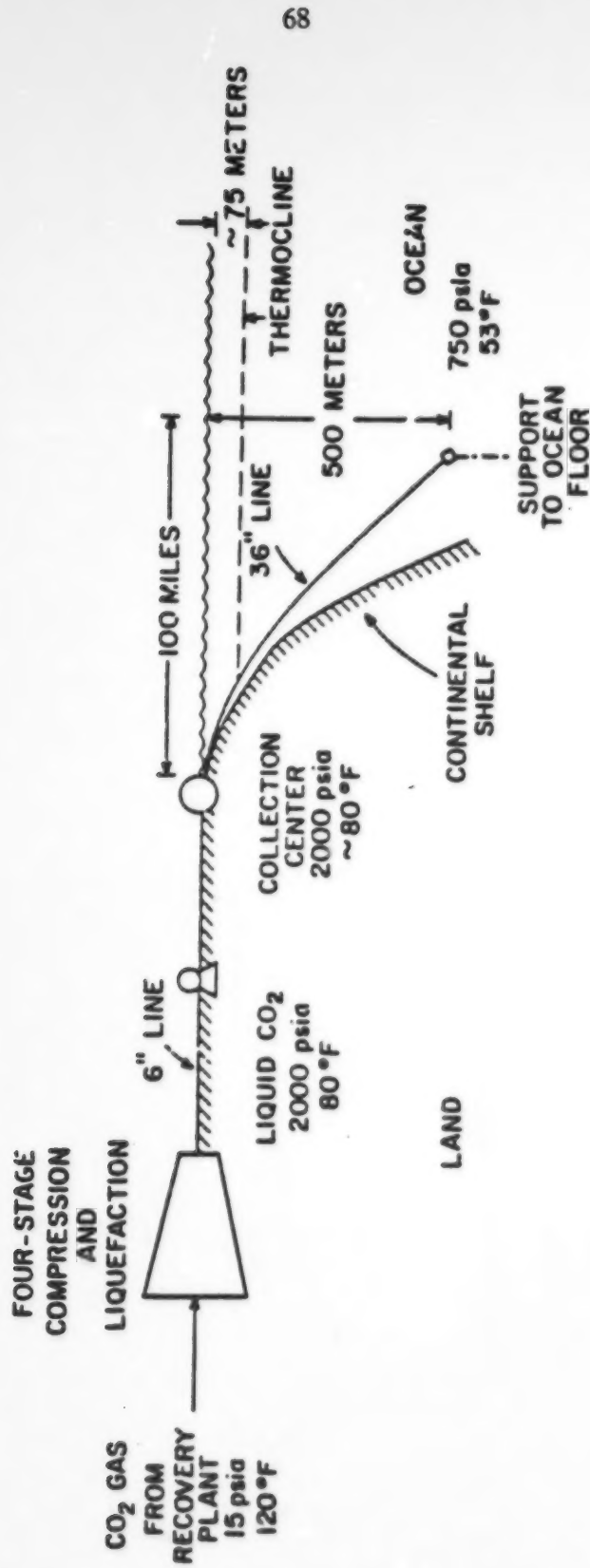


FIGURE 24. OCEAN DISPOSAL

Source: Steinberg, 1984.

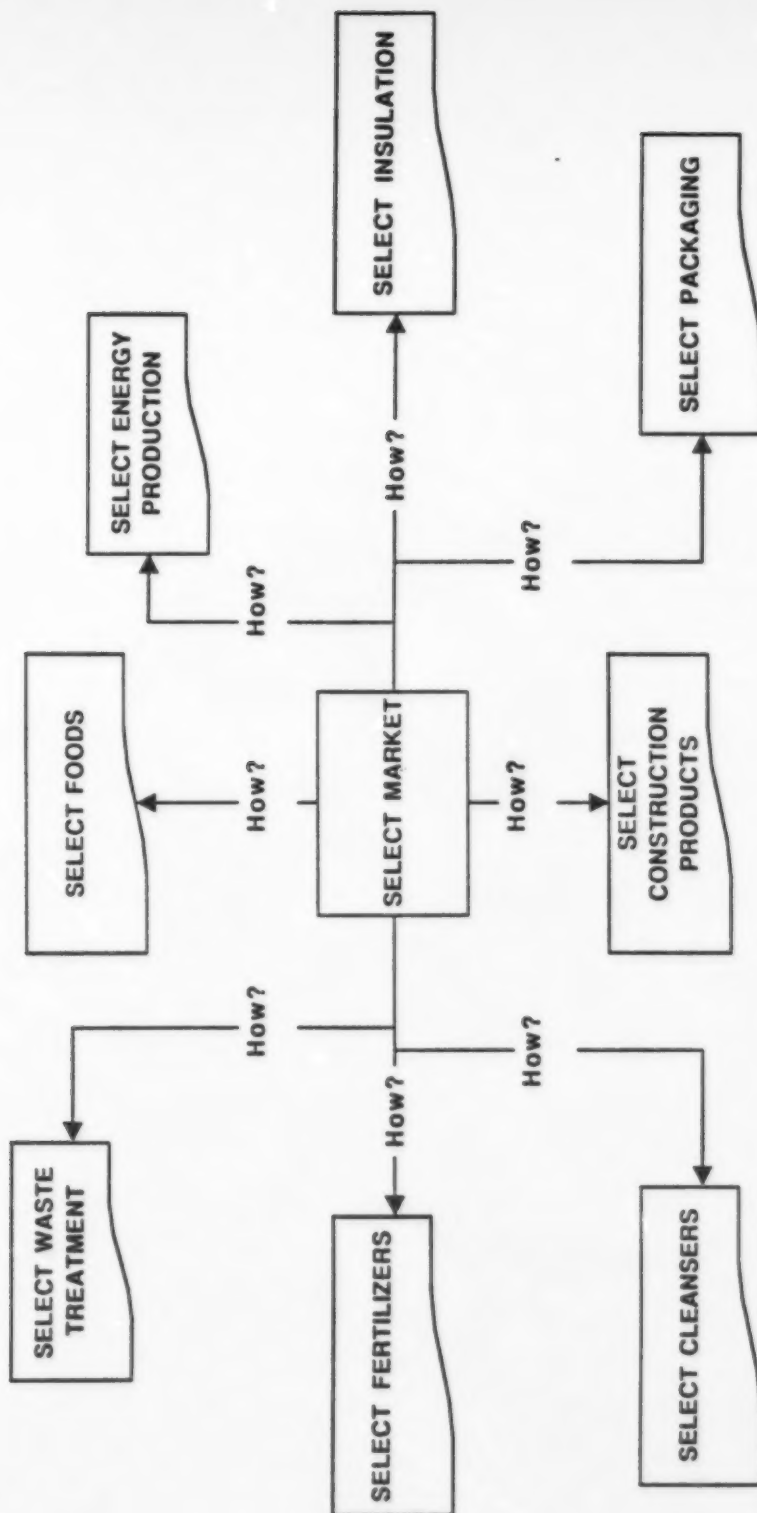


FIGURE 25. POTENTIALLY ATTRACTIVE MARKETS FOR CARBON DIOXIDE UTILIZATION

EOR is the primary potential market for carbon dioxide in Western Canada. Battelle has little to add to the knowledge of the Client Consortium. Battelle did note especially a detailed evaluation of the economics of carbon dioxide recovery and transportation for use in EOR (Anada, et al., 1983 and Wiggins, 1983). The special requirements for the supercritical carbon dioxide pipelines for this (and other) uses has been reviewed by Farris (1983). Instead, brine-derived chemicals are featured, because this is a somewhat controversial area in which Battelle has experience.

Brine-Derived Chemicals

The availability of magnesium-rich and calcium-rich brines were mentioned in the Disposal section of this report. They provide the potential opportunity for conversion to the following chemicals:

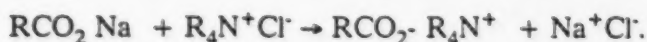
- (1) Precipitated carbonates for paper and plastics uses
- (2) Soda ash and sodium bicarbonate
- (3) Basic magnesium carbonate
- (4) Hydrochloric acid and chlorine
- (5) Bromine and iodine
- (6) Borates.

The precipitation of the carbonates from the chlorides is difficult, but the suggestions that were made in the Disposal section may produce sufficiently pure materials for sale. Thermal hydrolysis of magnesium chloride has the advantage of obtaining hydrogen chloride for sale. Alternatively, the HCl could be converted to chlorine by a non-electrolytic process (e.g., the Kel-Chlor process). The chlorine could be used to help in the recovery of bromine and/or iodine.

A sodium bicarbonate and soda ash process might be based on the magnesium bicarbonate that could be produced by reaction of magnesium oxide with carbon dioxide. The solution of magnesium bicarbonate can be exchanged for sodium ions on a

cation-exchange resin. The result is magnesium ion on the ion exchange resin and a solution of sodium bicarbonate. This bicarbonate can be heated to manufacture soda ash or crystallized and sold as such.

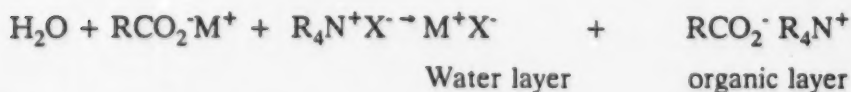
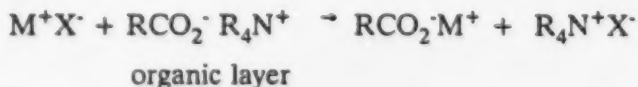
Grinstead Process. Battelle has considerable experience with a liquid ion-exchange process, known as the Grinstead process (refs). A kerosine solution of a Grinstead Salt results from the reaction of a "quat" of the sort used in fabric softening with a naphthenic acid sodium soap, as shown below:



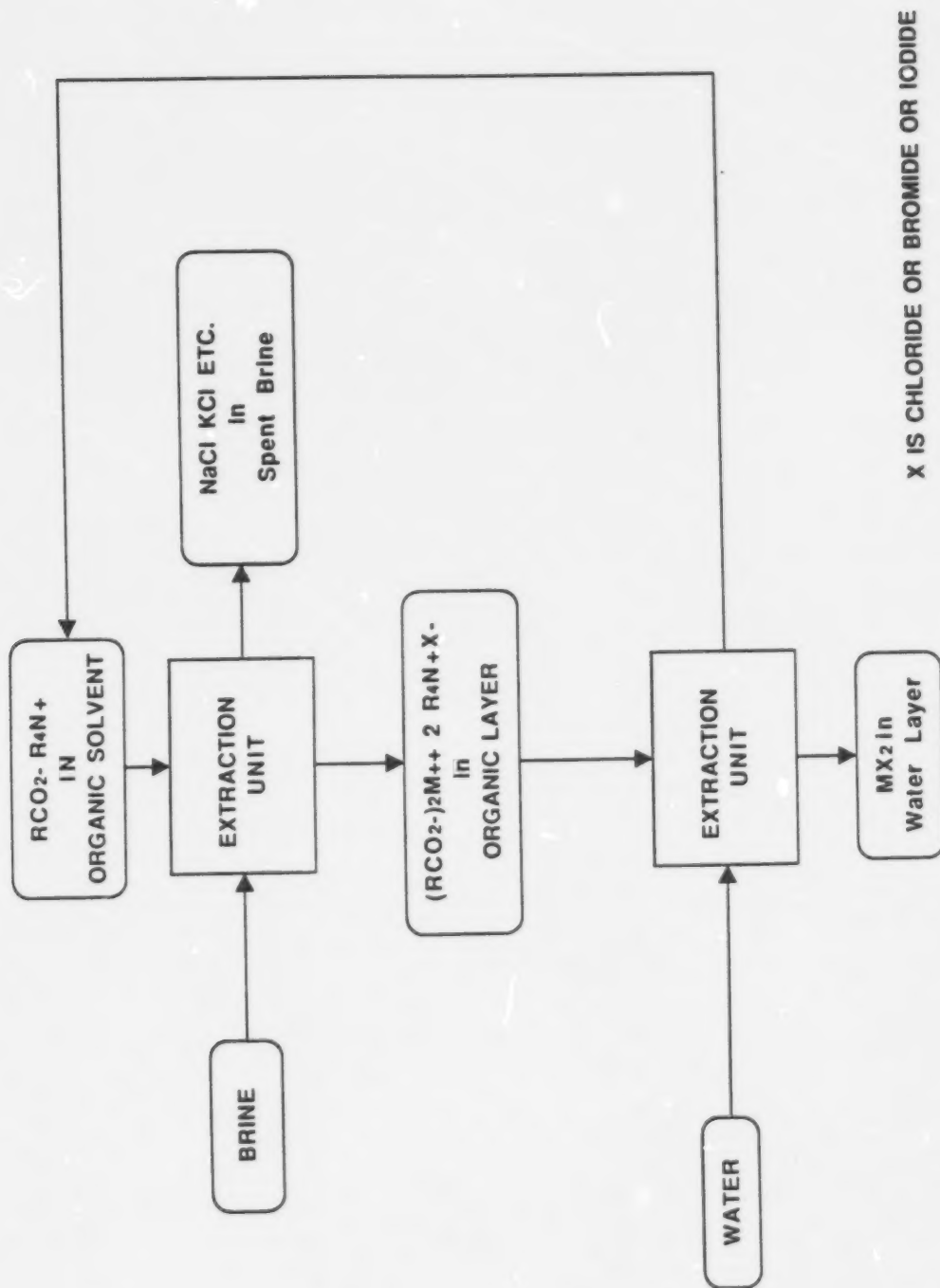
The fatty salt stays in the organic layer and the sodium chloride is washed away.

As shown in Figure 26, the Saskatchewan brine, such as the ones shown in Table 14, is extracted with this solution. The divalent cations (magnesium, calcium, and strontium cations) are extracted from the brine. We expect sodium, potassium, and other monovalent cations to stay with the aqueous layer, based on our experience in using this process on various Chilean brines. There is some evidence that bromides and iodides might also be extracted into the organic layer.

The salient feature of the Grinstead liquid ion exchange process is that recovery of the chemicals is achieved with water only! As shown below, the water reextracts the inorganic salts to form a concentrated solution of the salts directly. The fatty materials are converted back into the Grinstead Salt, ready for another cycle.



(M is shown as monovalent for convenience)



M IS MAGNESIUM OR CALCIUM OR STRONTIUM

FIGURE 26. GRINSTEAD PROCESS CONCENTRATES SELECTED IONS

Application of this process to Elk Point brines may or may not give useful results. The original concept was applied to Chilean nitrate brines where nitrate was accepted into the organic layer and chloride was rejected. Also, sulfate was rejected very well. Magnesium was well accepted into the organic layer and sodium was partially rejected from these sodium-rich brines. The Elk Point brines are quite different in that they do not have nitrate or sulfate. Sodium is relatively low and magnesium is already very high in concentration.

We visualize the venture as one in which a relatively small Grinstead extractor is coupled to a larger disposal unit. Thus, disposal and utilization are integrated, with the utilization process skimming the best ions from the mixture.

Construction Products

The annual production of carbon dioxide that could be captured for use is so large that only the biggest markets deserve consideration. The production of cement is conducted on the 100 million ton per year scale in the United States. That is the type of market that is worth considering.

In 1936, the American Chemical Society Monograph on carbon dioxide (Quinn and Jones, 1936) mentioned that carbon dioxide can be used to harden cement products. The cement products are highly alkaline (pH of 12.5 is typical). This free alkali can be neutralized by absorption of carbon dioxide. The method was applied to precast specialty products. Considering the huge production of cement products, there is a sizable potential market for carbon dioxide enhancement of concrete materials. What is needed are devices and processes to apply the carbon dioxide out at the construction site, not in a curing room.

The absolute upper limit would be neutralization of all of the lime in the cement (15 million tons per year). If only 10 percent were available on a technical and marketing basis, the market would be about 1.5 million tons per year. This would be a significant market that is similar in size to the 1986 market for carbon dioxide (Barer and Stern, 1986).

A related end use is the improvement of fiberboard and particle boards that are bonded with inorganic binders that are alkaline. There are deleterious reactions that occur between the alkaline binders and wood or other lignocellulose products (Moslemi, 1988 and Lipinsky, 1989). These products are usually made in hot presses. They could be equipped with carbon dioxide injectors.

Food Markets

The food industry is gigantic and in great need for the cooling that can be obtained relatively safely with liquid carbon dioxide or dry ice. The existing industry has recognized this situation and has developed the market in a dynamic fashion. Nevertheless, there are opportunities that might increase the market size considerably. These opportunities do not usually keep the carbon dioxide sequestered for long periods of time.

There is the opportunity to use the carbon dioxide/water clathrate as a gradual release or controlled release source of carbon dioxide for packaging applications. If an appropriate license from General Foods is obtained, a glassy material other than the carbon dioxide/water clathrate could be used.

New Topics

Many of the concepts that are discussed in the Disposal and Utilization sections of this report are topics that are new to most people. Some of the topics that are in this New Topics section may not be new to some of the readers. They are potential opportunities or topics to be evaluated prior to entry into carbon dioxide capture, disposal, or utilization.

Oxygen Via Thermal Swing Absorption

The key cost element in flue gas recycle combustion processes is that of oxygen enriched air. A recent DOE report (Jain, 1990) on "Thermal Swing Absorption

for Making Oxygen Enriched Combustion Air" reveals a process and a set of principles that could be extremely desirable for the Client Consortium.

The process is described in Japanese Patent 87-83,302 that has not been available at Battelle. Therefore, we have had to rely on secondary literature in this preliminary project (Jain, 1990). Jain's view of this process is shown in Figure 27.

The oxygen absorber is 2,4,6 trimesityl phenol. The rest of the solvent system includes t-butyl alcohol and potassium t-butoxide.

The process is very effective in recovering oxygen and rejecting nitrogen. Its key drawback is that it requires a temperature of 40 F for effective absorption. The DOE report authors believe that this implies a large capital outlay for a chiller and heavy expenditures for electricity to operate the chiller.

In the colder parts of Western Canada, this temperature of 40 F can be obtained routinely for much of the year. The penalty for operating somewhat less efficiently during the summer does not appear to be great. There is the opportunity to create frozen ponds during the cold season and also to limit use of this technology to those few areas in which it is feasible. Just as mining enterprises use only the geological formations that have sufficiently rich ores, so the carbon dioxide recoverers may be limited to those areas that have a special advantage, including climate advantage. The desorption temperatures are well within the limits that can be satisfied by waste heat at the power plant site.

The implication is that this concept may provide colder regions of Canada with a distinct potential advantage in oxygen costs that could enhance the viability of the flue gas recycle combustion process and IGCC power production. However, this small scale Japanese Patent example would have to be validated and possibly improved upon greatly in scale-up for this goal to be achieved.

Carbonated Ice

Some ten years ago, Battelle conducted a series of studies of CO₂ hydrates for the General Foods Company. This was part of a program to develop new snack

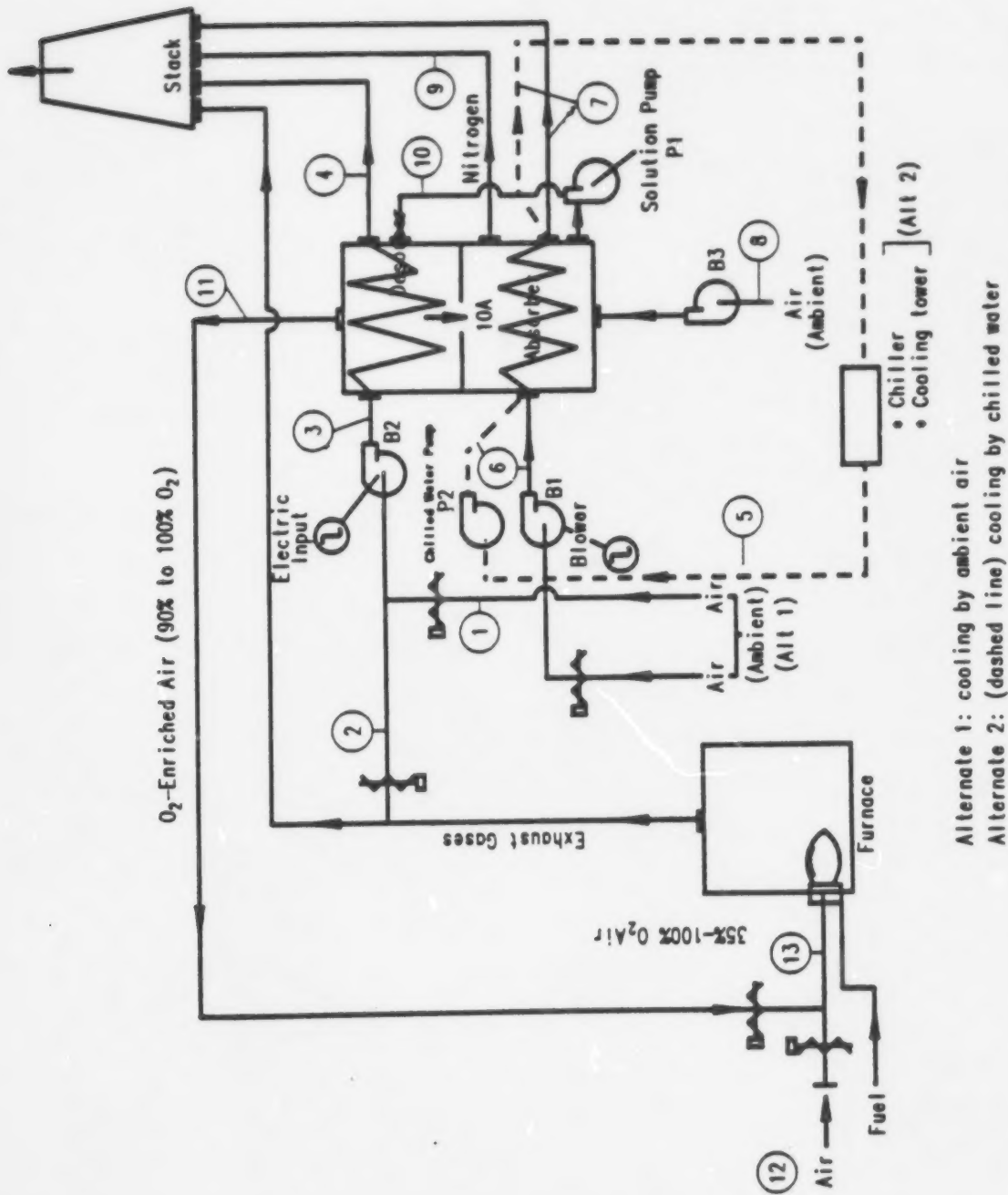


FIGURE 27. ON-LINE TSA-BASED OXYGEN ENRICHED COMBUSTION AIR PRODUCTION SYSTEM (Driven by Furnace Exhaust)

Source: R. Jain, "Assessment of Thermal Swing Absorption Alternatives for Producing Oxygen Enriched Combustion Air", DOE Report CE-04762T-H1 (1990).

products. The program resulted ultimately in a patented position for General Foods in both "Carb-ice" and inclusions of carbon dioxide in other glassy matrices, especially confectionery products. Carb-ice was intended to be stored in a freezer until use.

There is an extensive literature on CO₂ hydrates. The phase diagram (Figure 28) shows that the hydrate is stable at temperatures that are about at the freezing point of water and at about 10 atmosphere pressure. However, once carbonated ice is made, decomposition of the hydrate and diffusion of the carbon dioxide from the product are both slow so that it does persist at atmospheric pressure. Stability might be improved by applying pressure to the system.

The issues that concern carbonated ice as a carbon dioxide disposal method include:

- (1) Could carbonated ice be made on a large scale?
- (2) Can the half-life of the product be increased to a reasonable level by means of temperatures and pressures that are attainable in colder regions of Western Canada?
- (3) What are the favorable and unfavorable potential environmental impacts of storing large quantities of carbonated ice?

The key to making carbonated ice commercially is to use snow or small ice particles so that the carbon dioxide can diffuse in easily. The key to storing the product is to have large pieces through which the carbon dioxide diffuses out slowly. Most studies of carbon dioxide hydrates have been done on thin samples so that the complications that are involved in larger scale phenomena can be avoided. However, it is precisely these phenomena that may cause this concept to be valuable.

Large scale could also cause disadvantages. The breakdown of carbonated ice is exothermic so that there may well be a limit to the size of the particle so as to avoid dangers of an explosive decomposition.

We conclude that the use of moderate pressures and temperatures might make carbonated ice available as a potentially low cost storage method in cold Canada.

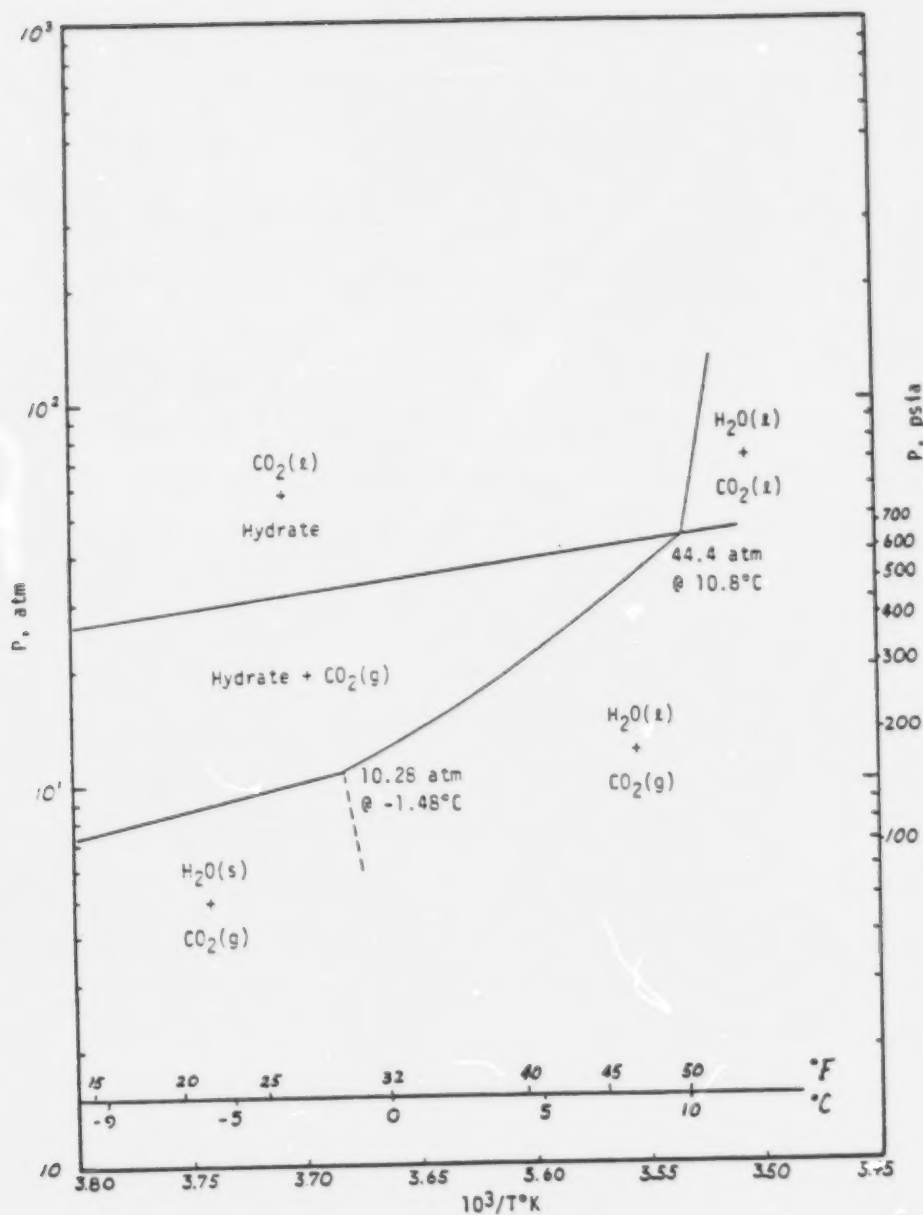


FIGURE 28. CO₂-H₂O PHASE DIAGRAM (Process Region)

Source: H-S. Chen, et al., "The Growth Rate of Ice Crystals: The Properties of Carbon Dioxide Hydrate", Syracuse University Report, NTIS NO. PB-217615 (1972).

However, there are potential limitations on the duration of storage and possible safety concerns. The area merits further research, with the understanding that it is highly speculative.

Polymers for Storage/Disposal

Polymers have some advantages over other materials for storage/disposal purposes. They may have desirable physical properties that allow them to be sold. The polymerization may be reversed under reasonable conditions to recover the monomers, if it proves to be desirable. Assuming that the polymer is a thermoplastic, there may be desirable ways to melt and pump or otherwise move the material.

The possible disadvantages of polymers are also to be considered. For example, the materials may degrade to carbon dioxide or something worse, they may lose their physical properties on prolonged storage, they may occupy a lot of space.

Additional opportunities that are more speculative arise in reinforced or filled plastics in which an alkaline material is used as a filler and carbon dioxide is permeated into the plastic so that calcium carbonate or other carbonates are made in situ. This is an analogue of biomineralization.

Carbon Dioxide Polymers. Battelle pioneered in development of polymers that use real carbon dioxide as a comonomer (Santangelo, 1987). Carbon dioxide copolymerizes with ethylene oxide or propylene oxide to yield a material that is about 50 percent carbon dioxide. This storability compares quite favorably with limestone which is 44 percent carbon dioxide.

This particular polymer has alternating groups that originate in the carbon dioxide and in the alkylene oxide. A new topic that we are addressing at Battelle is to change the ratio of carbon dioxide to alkylene oxide so that it is more than one. In the ultimate successful case, the alkylene oxide groups would be just end groups.

The parameters that would be varied would be the catalyst that facilitates the polymerization and the comonomer that is the initiator of the polymerization.

Miscellaneous Opportunities

Limitations in time and budget precluded investigation of several potentially attractive topics that were found in the literature search. They are summarized in Table 15, which also includes a leading reference.

Perhaps the most exciting is the use of supercritical CO₂ to replace VOC's (volatile organic compounds) in paints. The carbon dioxide is an excellent solvent for paints that are used in automotive applications where the high pressure conventional spray booths handle carbon dioxide well. This Unicarb® technology of Union Carbide has been licensed by BASF so that its success seems likely.

Although several groups are enthusiastic about the use of carbon dioxide as the feedstock for making methanol and synfuels, we believe that the hydrogen is the limiting reagent. In gasification to obtain hydrogen, plenty of carbon dioxide is formed.

Although the use of carbon dioxide to mold or foam plastics appears to be a small market, its use does appear to bring benefits to consumers.

Liquid carbon dioxide has been proposed for slurry pipelines, especially in areas in which water is in short supply. It could have prospects where the intention is to dispose of the carbon dioxide when it reaches its destination. Then, the transport aspect helps to pay for moving the carbon dioxide from the generating site to the disposal site.

Supercritical processing is a potentially valuable new technology. It might be applied to coal or petroleum commercially. We are not aware of its present status in this area.

FUTURE WORK

There are many opportunities to conduct worthwhile research and development activities in carbon dioxide capture, disposal, and utilization. It is especially desirable to plan coherent R&D programs with definite goals and milestones. Otherwise, the "research rat hole" effect will take over.

TABLE 15. MISCELLANEOUS CARBON DIOXIDE TOPICS

Concept	Big Usage of Carbon Dioxide	Profit Opportunity?	Favorable Impact on Environment	Reference
Solvents for paints to replace VOC's	no	yes	extremely good	Nielson, et al, 1990
Processing aid for injection molding of plastics	no	moderate	fair	Berens, 1989
Methanol and synfuels from carbon dioxide	yes	maybe	maybe	Chinchen, 1990
Liquid carbon dioxide slurry transport	no	yes	yes	Santhanam, 1983
Super critical CO ₂ for processing petroleum	no	yes	yes	Williams, 1981
Super critical CO ₂ for processing coal	no	yes	yes	Gangoli, 1977

The following outline is taken from suggestions that were scattered throughout this report. They should not be implemented haphazardly, but they are elements that could fit into a strategic plan.

I. Evaluate key processes in depth

A. Flue Gas Recycle Combustion

1. Oxygen processing
2. Oxygen accounting

B. IGCC Shift/CO₂ capture

1. Steam requirements

II. Develop key processes that seem attractive

A. If IGCC is attractive

1. build demo plant
2. Design to test various alternatives

B. If Flue Gas Recycle is attractive

1. build demo plant
 - a) Measure efficiencies
 - b) Simulate retrofit problems
 - c) Develop retrofit package

III. Develop basic information

A. CO₂ hydrates as materials

B. Magnesium brines as reactants for CO₂

IV. Explore potentially promising speculative opportunities

A. Magnesium chemicals

B. Brine as means of CO₂ disposal

C. Thermal swing oxygen production

D. Polymers from CO₂

1. Polycarbonates
2. Polyureas
3. Others

APPENDIX A: DATABASE

APPENDIX A: DATABASE

This database provides the List of References for this report and much more. The hard copy provides an alphabetical printout of the information on the disk that is included with the report. Using the disk, searches can be made for all references to specific organizations that performed or sponsored studies, for example. Keyword searches in the titles also can be useful. Because it is so handy to use, we have not encumbered the report with all possible citations.

The database can be sorted alphabetically or chronologically. Reports of the database holdings can be printed in various ways, as described by the suppliers of the software. This database can be combined with other databases that you already have or it can be the foundation for a new database.

The disk that is included with this report has two files on it, SYLK and EXCEL. It is provided in Syk format so that it can be used by a wide variety of machines, including the Macintosh. EXCEL for Windows® is the Microsoft database software that was used to prepare the disk that is included with the report. Those who have systems that are compatible with the original EXCEL for Windows® can use the EXCEL file and get some extra features.

APPENDIX B: EXCERPTS FROM BATTELLE MICROALGAL SYSTEM REPORT

APPENDIX B

EXCERPTS FROM BATTELLE MICROALGAL SYSTEM REPORT

Source: Final Report on Resource Assessment for Microalgal/Emergent Aquatic Biomass Systems in the Arid Southwest to Solar Energy Research Institute, December 23, 1982, by B. W. Vigon, M. F. Arthur, L. G. Taft, C. K. Wagner, E. S. Lipinsky, J. H. Litchfield, C. D. McCandlish, and R. Clark.

IV. CLASSIFICATION OF AVAILABLE AQUATIC SPECIES

This section has three major objectives:

- To describe candidate microalgae species which may be appropriate as producers of biomass and/or chemicals in systems to be located in the arid Southwest
- To discuss specific criteria for the future selection of candidate microalgae species for southwestern biomass systems
- To identify data gaps and suggest methods which may be useful in future programs to fill the data gaps.

During the search for available species and the development of criteria, several assumptions were made, including the following:

- Although both freshwater and marine species were considered, it appears from the previous tasks that aquatic biomass systems in the Southwest would best utilize saline water. Therefore, special emphasis was devoted toward describing the salt tolerance of the various species, when such information was available.
- The water to be utilized in the Southwest will probably be alkaline. Thus, unhydrated carbon dioxide probably will not be the major form of carbon supply, and carbonate or bicarbonate may serve as alternative carbon sources. Not all microalgae species are capable of utilizing hydrated forms of carbon dioxide.
- It generally was assumed that carbon supply will be the factor limiting microalgae production potential in the Southwest. Thus, carbon use efficiency is presented when possible.
- Southwestern water supplies may contain significant levels of potentially toxic compounds, such as arsenic or boron. Whereas most phycological studies have been conducted under laboratory conditions utilizing controlled media, an effort was made to find information on the response of microalgae to potentially toxic compounds.
- Temperature control may be an important concern for many species. Thus, temperature tolerance data are presented if possible.

- This effort was not to be a selection of species per se. Species selection efforts are being undertaken by other subcontractors for SERI. Our efforts were to be descriptive in nature.
- An attempt was made to describe the current knowledge concerning end-product formation (e.g. glycerin, lipids, etc.) by the various species, as well as biomass production.
- Finally, our approach to completing the objectives of this task included a literature analysis of what is and is not available regarding individual species. As this was a relatively short-term, low-level effort, the analysis is not comprehensive with respect to each species identified. In addition, the species described may or may not be potential candidate species; but their inclusion serves some specific purpose--such as showing metals toxicity data--which might be extrapolated to other species and thus are potentially useful data for researchers in species selection.

Criteria for Selecting Microalgae

In order for microalgae biomass systems to be successful, a number of useful microalgae species must be identified and characterized. A useful species is one which produces a desirable end-product and can be grown under the specific conditions employed in the biomass system. The specific conditions to consider include, in addition to selecting species which produce a useful product, the culture media including the chemical elements present and their concentrations; the source, amount, and purity of carbon; illumination; temperature; pH; salt concentration; and the physiological response of the algae to these parameters.

Culture Media

The culture media for microalgae biomass systems will be saline water of variable quality. Ideally, species would be found which not only tolerate the quality of the water to be used (trace metals, pH, salinity, etc.) but can extract their nutrient requirements without the need for additional supplementation. Laboratory maintained strains, although certainly essential for basic studies, may not reflect the water quality requirements of microalgae in situ. For this reason, indigenous strains may be desirable, assuming species can be isolated which produce useful products. Intuitively, the ideal species would be one that utilizes nutrients most efficiently, i.e., produces the greatest biomass or end-product while using the least amount of a nutrient.

Little information exists with respect to the responses of various species to potentially toxic trace elements. A specific criterion is to select useful species resistant to the quality and quantity of trace elements likely to occur in southwestern saline water. An alternative approach may be to acclimate useful species to the level of toxic elements likely to be encountered.

Carbon Source

Because CO_2 is the form of carbon which interacts with the major carboxylase, ribulose diphosphate carboxylase, unhydrated CO_2 is the major source of carbon for algal growth. Carbon dioxide enters the cell by diffusion, and for maximum growth rates, CO_2 concentrations should be as high as possible. In the Southwest, however, saline groundwater is alkaline and thus contains more carbonates and bicarbonates than unhydrated CO_2 . Not all microalgae species can absorb bicarbonate and those that do must convert the ion to unhydrated CO_2 for fixation via ribulose diphosphate carboxylase. Uptake of bicarbonate is an energy-requiring process and bicarbonate is converted intracellularly to CO_2 and OH^- by carbonic anhydrase. This enzyme does not occur in all microalgae but is prevalent in marine species; however, it is inducible in many species and may serve as an adaptation to low CO_2 , high bicarbonate, high pH.

For southwestern microalgae biomass systems, the status of carbon in the water will dictate which species will grow. The ideal species, and thus a criterion for selection, would possess carbonic anhydrase constitutively or inducibly, and thus could employ both hydrated and unhydrated forms of CO_2 . Laboratory studies in which CO_2 is bubbled through water as the source of carbon supplementation should employ high enough pH's to insure that bicarbonate is readily available.

Illumination

The ideal microalgae species for biomass systems would exhibit a very high photosynthetic efficiency, yet have an optimum growth rate when light is somewhat limiting. Several species described earlier produced the greatest cell yield when light was limiting; the optimum growth rate, as opposed to the maximum growth rate, has been discussed by Goldman (1980). The advantage to such a characteristic is that in a large pond system, irradiation intensity will be attenuated rapidly with increasing depth. This is often compensated for by agitation in order to expose as many individual cells as possible to the most irradiation. Species which grow optimally over the long term at less

than saturating irradiation may be adaptable to a pond in which the need for (energy intensive) agitation is greatly reduced.

Temperature

Southwestern saline pond systems will be subjected to extreme fluctuations in temperature, from less than 0 C to greater than 40 C. In lieu of some form of temperature control, which may be very costly on the scale proposed for pond systems, species should be selected which exhibit extreme tolerance to temperature fluctuations. The ideal species would remain metabolically active at temperatures below freezing and up to 40 C or greater. A species which produces a desirable product yet is killed at moderately warm temperatures (e.g., 30 C) may find limited use in southwestern biomass systems.

pH

Groundwater supplies in the Southwest are likely to be alkaline due to the calcareous nature of the soils and the salinity of the water itself. Microalgae may tolerate extremes in pH as high as 13.5; Chlamydomonas acidophila can be cultured at pH 2.0 in vitro and may survive pH 1.0 in situ. Some species of Chlorella have a lower tolerance limit of pH 2.0, while other Chlorella have a lower limit of pH 5.5. Thus, it is not easy to generalize optimum conditions with respect to pH, and candidate microalgae must be delineated individually with respect to hydrogen ion tolerance. An important consideration in biomass programs, in which CO₂ may be the limiting factor, may be the use of inorganic carbon other than CO₂, e.g., bicarbonate. As discussed previously, bicarbonate concentrations are increased at high pH, and carbonic anhydrase is active also at these higher pH's. Marine species are adapted to these higher pH levels, and the maintenance of alkaline pH may be the best option for maximizing carbon use efficiency.

Therefore, an important criterion for screening potentially useful microalgae species is that they should be able to tolerate alkaline pH. Those species screened on the basis of carbon use (bicarbonate) should be adaptable

to alkalinity. However, as shown in the section on species descriptions, alkaline pH in the presence of high ammonium salts may result in high concentrations of free ammonia, and thus toxicity. It may be necessary to screen species also on the basis of ammonia toxicity, or control the ammonium salts in microalgae ponds.

Salinity

Water ranging from fresh to salt-saturated will probably be exploitable for microalgae aquatic biomass systems. This conclusion is based in part on the ecology of halophilic and halotolerant microalgae, such as species of Dunaliella. This genera reportedly is the only eukaryotic algae which grows in extremely saline lakes.

The Great Salt Lake in Utah has been studied fairly extensively in terms of microbial ecology and may offer an ideal site from which to gain perspective on the saline culturing of microalgae. This lake is approximately 10 m deep, 116 km long, and 50 km wide, and is divided approximately in half by an east-west traversing causeway. Fresh water enters only in the southern half of the lake and migrates slowly to the north half. The result is a salinity gradient ranging from less than 10 percent (w/v) NaCl in the southern half to greater than 30 percent (w/v) NaCl (saturated) in the northern half. The elevation of the lake is 1280 m and so it is subject to annual air temperature variations of from -30 C to 40 C. The water temperature, however, varies from 5 C to 30 C for the most part; in isolated shallow areas of little slope, the water temperature can reach 50 C. In addition, the water and sediments reportedly contain Li, B, Cu, Zn, Pb, Cd, and As in unusually high concentrations (Brock, 1975).

Interestingly, Dunaliella spp. are found throughout the salinity and temperature ranges of the Great Salt Lake. Whereas some other prokaryotic and eukaryotic algae may tolerate some degree of salinity, only Dunaliella can tolerate salt-saturated conditions. The optimum salinity for Dunaliella, however, is about 15 percent (v/v) NaCl, much lower than its tolerance limit. Thus, Dunaliella dominates at higher salinities not because it thrives optimally under such conditions, but because it out-competes all other species.

It should be apparent that there are naturally occurring species capable of producing useful products and which can tolerate various levels of salinity. Microalgae species need to be selected which will span the salinity range expected. A feasible system may be a series of ponds, each of a slightly greater salinity and each with a differently adapted algae.

Physiological Responses of Algae

The ideal microalgal species would produce a valuable product at a rate which can be controlled by external variables such as temperature, salinity, illumination, or nutrient level. Progress has been accomplished with a few species (discussed earlier), but considerable work needs to be done on other species. Microalgae species need to be screened on the basis of their responses to environmental parameters so that their production can be easily controlled in large-scale systems.

Summary

To summarize the above discussion, the ideal microalgae species for biomass systems in the Southwest would exhibit the following characteristics:

- It would produce a highly desired product which, ideally, would be easily recoverable.
- It would utilize nutrients and water efficiently and would show some tolerance to trace metals.
- It would be able to utilize alternative sources of carbon, such as bicarbonate and low quality CO₂.
- It would show optimum growth and/or production of the desired product at less than saturated irradiation.
- It would have a broad temperature tolerance range, possibly from 0 to 40 C.
- It would prefer a neutral to slightly alkaline pH.
- It would possess a high tolerance to saline water.

- It would exhibit predictable responses to changes in growth conditions with the intent to alter the rate of formation or quality of end product.

These ideal characteristics also illustrate some of the criteria which should be employed for screening potentially useful species of microalgae.

Information Needs

It should be quite apparent that there are very few species which have been characterized well enough to be employed in a microalgae biomass system. Data are sorely lacking with respect to those species which produce desirable products and which tolerate the environmental and cultural conditions of pond systems in the Southwest. A systematic search for potential species should be performed, based in part on the criteria established in the previous section. Basic data such as carbon use efficiency, water use efficiency, photosynthetic efficiency, tolerance to pH, salinity, temperature, and trace elements, and response to irradiation are necessary for each species. The most important criterion, however, is to determine whether a given species produces a potentially useful product. Based on this initial screening, the other criteria can be applied systematically.

Programs are currently underway, sponsored by SERI, to identify candidate species. A part of these efforts will examine species indigenous to the Southwest, and then characterize them with respect to chemical composition, growth requirements, etc. The current efforts for SERI might benefit if the previous list of criteria, or an expanded version of the criteria, were applied to each species.

In Section VI, more specific research needs have been identified. To summarize the data gaps, the information which should be compiled on each potentially useful species is shown in Table IV-9.

TABLE IV-9. INFORMATION NEEDS FOR MICROALGAE SPECIES
POTENTIALLY USEFUL FOR AQUATIC BIOMASS SYSTEMS

-
- Useful product obtained
 - Carbon use data
 - use efficiency
 - chemical form(s) required
 - pH data
 - tolerable range
 - optimum
 - Temperature data
 - tolerable range
 - optimum
 - effect of changes on end-product composition
 - Salinity data
 - tolerable range
 - optimum
 - effect of changes on end-product accumulation
 - Irradiation data
 - maximum response
 - optimum response
 - long-term growth rate
 - use efficiency
 - effects of changes on end-product accumulation
 - Other data
 - water use efficiency
 - ease of maintenance
 - response to potentially toxic trace elements
-

TABLE V-1. CO₂ REQUIREMENTS AND COST FOR MICROALGAL SYSTEMS

$$1,000 \text{ ha} \frac{40 \text{ tons algae}}{\text{hectare}} = \frac{2 \text{ lbs CO}_2}{1 \text{ lbs algae}} = 80,000 \text{ tons CO}_2/\text{year}$$

$$80,000 \text{ tons} \frac{1.63 \times 10^4 \text{ SCF}}{\text{Ton}} = 1.304 \times 10^9 \text{ SCF} = 1.3 \text{ million MSCF CO}_2/\text{year}$$

Where

SCF = standard cubic feet

MSCF = thousand standard cubic feet

Since costs range from \$1.25 - \$3.00/MSCF, (Chemical Week, 1982), the cost for CO₂ for the project will range from:

$$1.3 \text{ million CO}_2/\text{year} \times \$1.25/\text{MSCF} = \$1.6 \text{ million/year for CO}_2 \text{ to}$$

$$1.3 \text{ million MSCF CO}_2/\text{year} \times \$3.00/\text{MSCF} = \$3.9 \text{ million/year.}$$

This is equivalent to about \$50 per oven dried ton of algae.

Carbon Dioxide Supply

Production of microalgae on a scale that is significant to the United States in terms of energy substitution either in fuels or chemical feedstocks and in terms of land area devoted to this means of biomass production requires supplementation of atmospheric carbon dioxide with additional carbon resources. This additional carbon might be supplied by gaseous carbon dioxide from wells, carbon dioxide contained in natural gas, gaseous carbon dioxide contained in flue gases, bicarbonate minerals, and carbonate minerals. Other sources of organic carbon include sewage, food processing waste, and similar materials.

Many areas of the southwestern United States that have desirable solar insolation and water will not have an adequate supply of inexpensive carbon dioxide. Therefore, carbon supply is an excellent screening tool in mapping the specific locations at which it may be practical to produce algal-biomass on a significant scale.

Massive supplementation of atmospheric carbon dioxide with fossil carbon dioxide (such as the CO_2 that is contemplated for use in enhanced oil recovery) implies a limitation to the size of the algae biomass production units. Because CO_2 injection into oil fields produces such a rich reward of energy through enhanced oil recovery, CO_2 that can be used for this purpose is relatively valuable in energy terms and in dollar terms. If algae production is to compete with enhanced oil recovery, the end products must be sufficiently valuable to justify the algae use. This consideration tends to tie algae to chemicals or fuels with unusually high selling prices. The economics also can be improved by making this supply of carbon to algae a part of an overall system that can result in a sharing of carbon supply costs. Typical examples would include scrubbing CO_2 from natural gas that would otherwise be too contaminated with CO_2 to be worth a high selling price and then using the CO_2 thus recovered to grow algae. In this scheme, the cost of CO_2

could be shared between the algae venture and the associated methane production venture. For this type of venture, the algae might even be anaerobically digested to methane and CO_2 so that the only product that had to be sold was methane.

Another example of sharing costs would be flue gas utilization in which stack gas cleanup could be combined with algae production. Stack gases are not suitable for enhanced oil recovery, thus this approach has less competition.

The development of new aluminum oxide resources in the United States is a matter of considerable concern, because bauxite is available from a limited number of suppliers. The mineral dawsonite contains both alumina and sodium bicarbonate. The cost of isolating the alumina could be shared with the production of carbon dioxide from this resource.

Carbon Supply

The previous discussion has pointed out that CO₂ reservoirs exist in the southwestern United States and that use of this CO₂ supply for algal production will have to compete with its use in enhanced oil recovery. The quantity of CO₂ present in the atmosphere (about 0.03 percent) is too low to support large-scale algal production, given the present state of knowledge on carbon source requirements for algal growth and the means to contact the algae with gases. Consequently, additional CO₂ must be supplied.

Theoretical values for carbon requirements for algal growth can be calculated based on the chemical composition of the cells (Goldman, 1980). However, the available data on CO₂ requirements for actual operating algal systems vary widely. For example, for Chlorella production in Taiwan, 4.8 Kg CO₂ were required per Kg dry weight of algal cells while in the Indian-West German project on cultivation of Scenedesmus, the minimum requirement was 1.6 Kg CO₂ per Kg (dry weight) of cells (Kawaguchi, 1980; Becker and Venkataraman, 1980).

Further research is needed on the factors affecting the efficiency of CO₂ utilization by species of algae selected for use in large-scale culture systems. Also, operating data are needed on CO₂ conversion by algal cultures to cell products.

Research is also needed on factors that limit gaseous CO₂ availability to and uptake by cells of dependable algal species in mass open culture systems at high biomass densities [above 1-2 g/l (dry weight)]. These

factors include investigations of (1) diffusional boundary layers around algal cells that limit CO₂ diffusion, (2) effects of ionic strength, (3) effects of ionic strength and pH, and (4) the effects of improved mixing systems under given light intensities. The Brune and Novak model of the carbon-limited growth response of algae in continuous culture systems needs to be verified experimentally (Brune and Novak, 1981).

In Israel, flue gases have been used as a form of CO₂ for growing Spirulina platensis in channel cultures (Berend, Timovitch and Allian, 1980). However, there is a lack of published information on actual efficiency of CO₂ utilization from flue gases by algae.

Experimental studies should be conducted to determine the conditions giving the best utilization of CO₂ from flue gases. The extent to which flue gas constituents such as H₂S, SO₂, SO₃, CO and CH₄ are inhibitory to various algal species is not well understood. There is a need for an investigation of the levels of these impurities that can be tolerated by algae when flue gas is used as a CO₂ source. Also, methods and costs for reducing the concentrations of these impurities to acceptable levels, e.g., scrubbing should be evaluated.

The possibility of integrating natural gas sweetening processes with algal production is an interesting possibility. The removal of CO₂ from CH₄/CO₂ mixtures with amines, followed by steam dissociation of the amine should be investigated. The CO₂ produced should be used in experimental algal culture systems. The results of these studies should provide data to determine if an integrated natural gas sweetening-algal production process merits further attention.

CO₂ availability to and utilization by algae might be enhanced by novel methods for contacting the gas with the algal cells. The application of mineral flotation methods should be investigated to determine if improved cell surface gas contact and improved CO₂ utilization can be achieved.

The use of carbonate-bicarbonate sources of carbon has been investigated for the production of Spirulina maxima biomass in naturally alkaline waters in Mexico (Durand-Chastel, 1980). However, there is no indication in the published literature that a NaHCO₃ carbon source has been evaluated for growing algae that produce high-valued chemicals, such as glycerol or

carotenoids. Experimental studies should be conducted to determine if algae, such as those in the genus Dunaliella that produce glycerol and B-carotene could utilize NaHCO_3 - Na_2CO_3 from mineral sources in such a process. These organisms are salt-tolerant and produce glycerol under brackish water conditions (Ben-Amotz and Avron, 1980). Spirulina platensis can be grown in alkaline waters. Studies in Israel have shown that this organism can produce B-carotene, xanthophylls, chlorophyll, and phytocyanin and enzymes or co-factors such as ferridoxin, cytochromes, etc. (Tel-Or et al., 1980) The possibility of improving algal cultures known to produce high valued chemicals by strain selection or genetic modification should be investigated.

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